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Total Recycle Systems for Petrochemical Waste Brines Containing Refractory Contaminants

Dow Chemical Co, Freeport, TX

Prepared for

Robert S Kerr Environmental Research Lab, Ada, OK

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The combined electrodialysis-reverse osmosis system is not considered economically feasible when applied to industrial wastewaters containing relatively high concentrations of salt.

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques, and new technologies through which optimum use of the Nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this research through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in ground water; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control, or abate pollution from the petroleum refining and petrochemical industries, and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

This report contributes to the knowledge essential if the EPA is to meet the requirements of environmental laws that it establish and enforce pollution control standards which are reasonable, cost effective, and provide adequate protection for the American public.

W. C. Galegar

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ABSTRACT

Petrochemical wastewaters containing relatively high concentrations of salt and refractory organics were selected to study their feasibility for total recycle. A combination of reverse osmosis and electrodialysis was operated as a hybrid system using the pretreated wastes, to produce reusable water and a concentrated brine.

Stream 1, characterized by a salinity of 1.4 percent NaCl when neutralized, contained an average of 0.5 percent organic amines and ammonia. It was found to contain enough silica to foul the membranes. Stream 2, contained 4.5 percent dissolved solids and precipitated aluminum salts when neutralized with acid. Its organic content of aromatics averages 90 mg/l of TOC.

A total recycle system for Stream 1 is composed of ammonia stripping, carbon adsorption and recovery of the organic amines, neutralization and silica removal before the ED-RO hybrid. For a 1 MGD Stream 1 waste treatment facility the estimated capital cost is $6,949,550 (1975 dollars) and the estimated operating cost is $5,291,700 per year. The carbon adsorption step has an estimated operating cost of $2,358,000 recovering organics suitable for recycle at an estimated value of $3,000,000 per year.

A total recycle system for Stream 2 is composed of neutralization, settling and centrifugation to recover $Al(OH)_3$, and carbon adsorption with thermal regeneration before the ED-RO hybrid. For a 1 MGD Stream 2 treatment facility, the estimated capital cost is $9,170,000 and an operating cost is $2,293,700 per year. No valuable organics are recovered from this stream.

The combined electrodialysis-reverse osmosis system is not considered economically feasible when applied to industrial wastewaters containing relatively high concentrations of salt.

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SECTION 1

INTRODUCTION

Petrochemical process waste streams have varied chemical constituents. Some components are easily degradable and are amenable to biological treatment processes, some are not, while others are toxic to living matter. Consequently, an optimal balance between physical, chemical, and biological treatment must be considered in the development of total recycle and reuse master plan.

Most of the highly contaminated waste streams from petrochemical plants originate from process areas, including condensed steam from stripping operations, wash waters from drum cleaning operations, water formed or eliminated during various reactions and other similar in-process sources. A variety of contaminants are found in these waste waters, including unreacted feed stock chemicals, products, by-products, side-products and spent catalytic materials.

Caustic washes and acidic washes are frequently used to extract or neutralize acidic and basic components from process streams resulting in a waste stream containing inorganic salts in addition to the organic components.

Refractory (non-biodegradable) pollutants are of special interest because of their possible adverse effects and their persistence in the environment. The establishment of more stringent effluent quality standards will necessitate greater utilization of advanced treatment processes. At the present time, however, application of advanced treatment methods to petrochemical wastes has been limited. In addition, there are many unanswered questions regarding the treatment and/or recovery of chemicals resistant to biodegradation. Although the salvage of unreacted chemicals and recovery of usable products and by-products from waste waters is desirable, economic considerations have usually dictated treatment rather than recovery.

The evaluation and development of advanced chemical and physical treatment methods, and the determination of the proper integration of selected unit operations to constitute an optimum waste treatment system is necessary. A system of total recycle involves both component recovery and water reuse.

The types of physical and chemical treatment processes commonly investigated for the treatment of petrochemical wastes include stripping, adsorption, extraction, ion exchange and oxidation. Because these wastes almost invariably contain dissolved salts, desalination methods such as reverse osmosis and electrodialysis are required to concentrate the inorganic components of the waste streams (total recycle system).

The Dow Chemical Company has investigated electrodialysis as a process for the concentration of desalination plant brines for the Office of Saline Water. Under OSW Contract No. 14-30-2676, Dow designed and built an electrodialysis brine concentrator which operated at Roswell, New Mexico from February 1971 to August 1972. The Dow testing concluded under Contract No. 14-30-3031 with the combined operation of a hybrid reverse osmosis-electrodialysis pilot plant from August 1972 to May 1973.

Results of the operation of the Roswell facility showed that reverse osmosis and electrodialysis can be utilized together to produce desalted water and concentrated brine. For a variety of feed water salinities, the reverse osmosis-electrodialysis system can economically achieve a high degree of separation between the water and the salt.

The capabilities of reverse osmosis and electrodialysis complement each other well. Reverse osmosis produces a low salt product quite well from brackish water but is a poor brine concentrator. Electrodialysis easily produces a ten to fifteen-fold concentration of salt in a single stage but often requires several stages operated in series to produce a satisfactory desalted water quality. The operation at the Roswell plant demonstrated that the combination of electrodialysis and reverse osmosis can be used to simultaneously concentrate the reject wastes from the reverse osmosis unit to more than 20 weight percent sodium chloride and produce reusable product water.

A general schematic of the total recycle system studied is shown in Figure 1. The main objective of this investigation was to apply the necessary combination of these unit operations to each of the simulated wastes so as to approach a total recycle system.

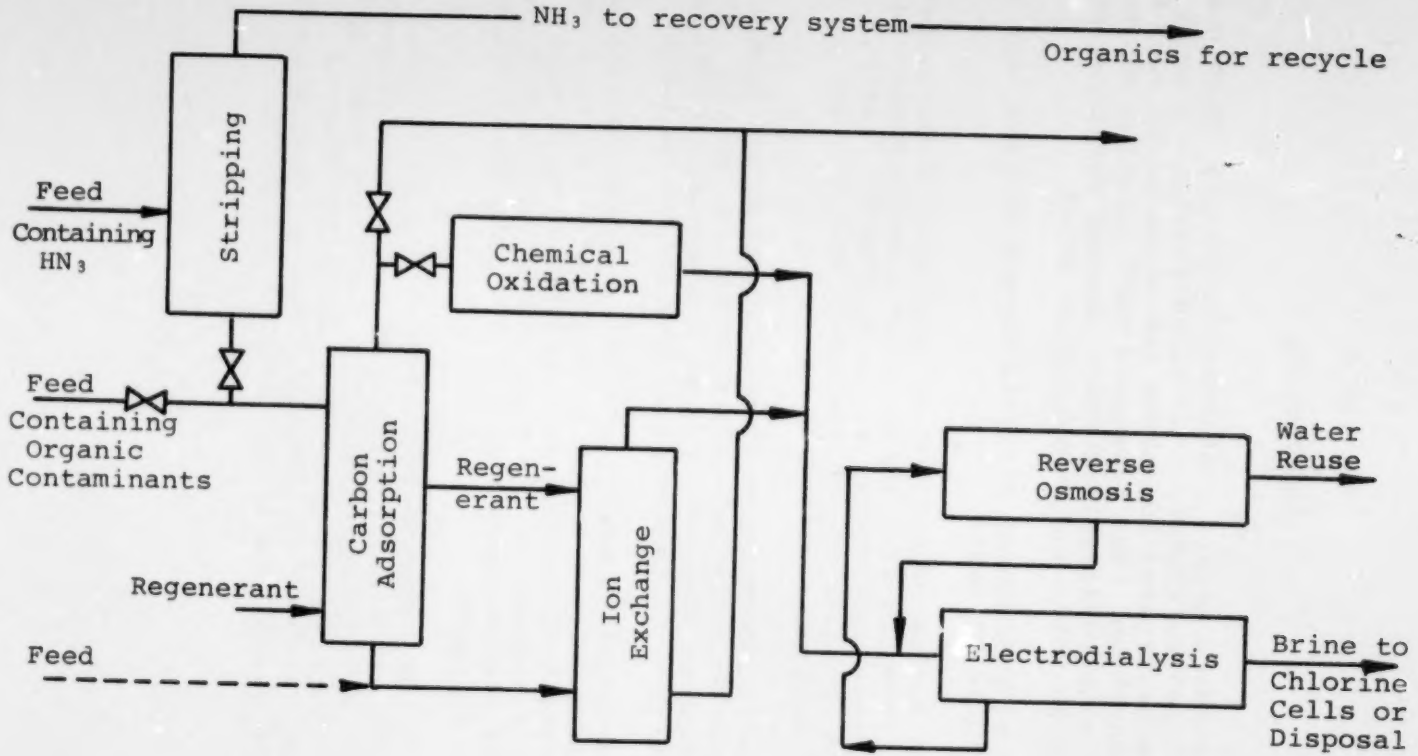

Figure 1. GENERAL SYSTEMS ENGINEERING - TOTAL RECYCLE SYSTEMS

SECTION 2

CONCLUSIONS

Petrochemical waste waters containing relatively high concentrations of salt and refractory (non-biodegradable) organic contaminants can be treated to remove the organics by such methods as carbon adsorption. The remaining salt solution can be concentrated by an electrodialysis-reverse osmosis desalination process to produce fresh water and concentrated brine.

For the type of petrochemical waste waters studied, the following conclusions could be made:

1. The carbon adsorption of relatively high concentrations of organics from petrochemical waste waters is technically achievable, but economically feasible only if the organics can be recovered and recycled to the production facility.

2. Low concentrations of organics that are highly adsorbable on activated carbon cannot be removed from petrochemical waste waters, at a reasonable cost, because of the cost of regenerating the carbon thermally.

3. The combined electrodialysis-reverse osmosis system is technically a feasible desalination process that produces both concentrated brine and fresh water. Pretreatment of the waste water is required to remove any contaminants that can foul the membranes of the ED or RO units.

4. For the range of salt concentrations (1.5-4.5 percent NaCl) studied, the combined electrodialysis-reverse osmosis system capital and operating costs were found to be high and the return from the value of the brine and fresh water produced would not economically justify the investment in the process equipment.

SECTION 3

RECOMMENDATIONS

It is recommended that:

1. In-place regeneration of activated carbon be investigated for each particular waste water in order to reduce the cost of the carbon adsorption treatment.

2. Whenever possible, waste waters containing high salt concentrations should be recycled without desalination and/or concentration.

3. The application of a combined electrodialysis-reverse osmosis system would be limited to salt concentrations and situations where it is economically feasible.

SECTION 4

WASTE WATERS SELECTION AND CHARACTERIZATION

Five waste waters were initially considered for the demonstration of the total recycle concept. All were brines resulting from the production of petrochemicals and contained various organic contaminants known to be refractory to biological oxidation. An in-depth characterization survey was done on the two waste waters selected for demonstration. The results of the study of the first two waste waters and a cost analysis of electrodialysis-reverse osmosis treatment of these brines led to the decision to minimize characterization of the last three waste waters because these contained much higher salt concentrations and were much less adaptable to the total recycle system concept.

Procedures used for analysis of the various parameters in the waste waters were taken, for the most part, from standard analytical reference texts (EPA, 1971; APHA et al, 1971). Chromatographic methods were developed as required to measure specific organic constituents of the waste streams.

In all cases, waste water was sampled during normal operation of the units producing the waste water. Sampling was designed to obtain daily representative samples. Where required, multiple daily samples were taken and composited.

The principal objective of the characterization was to determine if any parameters or contaminants were present that would affect the operation of the electrodialysis-reverse osmosis (ED-RO) recycle system. Such contaminants as calcium, magnesium and sulfate ions, silica, suspended solids, organic acids and bases, and some nonpolar hydrocarbons could be expected to foul the membranes used in the ED-RO recycle system. If these types of contaminants are present in the waste waters, it is expected that pretreatment of the brine would be required.

"Methods for Chemical Analysis of Water and Wastes", Environmental Protection Agency, Water Quality Office, Analytical Quality Control Laboratory, Cincinnati Office, 1971.

"Standard Methods for the Examination of Water and Wastewater", Thirteenth Ed., American Public Health Association, Washington, D.C. APHA, AWWA and WPCF, 1971.

STREAM 1 - CHARACTERIZATION

Stream 1 is an organic production waste water stream containing nitrogenous organic compounds. The summary of the inorganic constituents, organic constituents, and trace metal concentrations of Stream 1 are given in Table 1.

The results indicated that the waste water might need treatment for removal of silica, amines, and possibly calcium, magnesium, and sulfate ions before being processed by the ED-RO recycle system. Approximately 70 percent of the total organic carbon (TOC) and 83 percent of the organic nitrogen were accounted for by gas chromatographic (GC) analysis. It is known, however, that higher molecular weight diamines that cannot be determined by GC analysis are present in the waste water.

STREAM 2 - CHARACTERIZATION

Stream 2 is a petrochemical production waste water. The summary of the inorganic constituents, organic constituents, and trace metals concentrations of Stream 2 are given in Table 2.

Approximately 95 percent of the total organic carbon (TOC) was accounted for by the benzene and ethylbenzene found by the gas chromatographic analysis. The results indicated that the waste water will probably have to be treated for removal of the aluminate ion, the aromatic hydrocarbons and possibly the silica.

Table 1. INORGANIC AND ORGANIC CONSTITUENTS - STREAM 1

Parameter	(Concentrations in mg/l) Minimum	Maximum	Average
pH	12.3	13.2	12.6
Total Alkalinity as NaOH	2,426	21,646	10,550
NaOH	1,653	12,160	5,190
Total Dissolved Solids (TDS)	2,380	15,770	6,990
Suspended Solids	18	84	37
Ammonia-Nitrogen	30	300	157
Inorganic Carbon (IC)	8	64	24
Silica	10	80	45
Chloride ion	74	1,015	433
Sulfate ion	27	40	35
Total Organic Carbon (TOC)	903	3,843	1,824
Organic Nitrogen	1,110	3,460	2,046
Calcium			20
Magnesium			8
Iron			1.1
Cu, Zn, Mn, Cr			0.2
Ni			0.4
Al			0.8

Table 2. INORGANIC AND ORGANIC CONSTITUENTS - STREAM 2

Parameter	(Concentration in mg/l) Minimum	Maximum	Average
pH	11.3	12.8	12.0
Total Alkalinity as NaOH	1,600	9,680	4,947
Total Dissolved Solids (TDS)	20,800	62,500	42,320
Suspended Solids	2	58	31
Inorganic Carbon	2	968	166
Silica	nil	8.4	4.7
Chloride Ion	10,075	29,500	21,400
Sulfate Ion	nil	nil	nil
Color-APHA units	20	90	45
Aluminum Ion	325	920	680
Total Organic Carbon (TOC)	21	197	86
Total Oxygen Demand (TOD)	74	329	126
Calcium			7.6
Magnesium			1.0
Iron			0.7
Cu, Zn, Mr, Cr, Ni			1.6

SECTION 5

STREAM 1. TOTAL RECYCLE SYSTEM

Stream 1 was selected to be studied in detail for the applicability for recycle as shown in Figure 1. The objective was to investigate the required combination of unit operations that would approach a total recycle system. The reverse osmosis and electrodialysis operating as a hybrid to produce reusable water and a concentrated brine suitable for recycle is the principal ionic management of the advanced treatment system. Unit operations preceeding the RO-ED system are necessary for removal of any constituent that interferes with the operation of the RO or ED units, and if possible, for the recovery of valuable constituents to improve the economics of the recycle system.

A. PRETREATMENT STUDIES

The characterization of Stream 1 indicated that at least four steps would be necessary before the waste water could be treated by the reverse osmosis-electrodialysis process. These steps are ammonia removal and recovery, amine removal and recovery, neutralization and possibly silica removal. Ammonia removal is necessary to prevent the ammonia from appearing in the product water or the brine, and recovery is desirable. The amines must be removed because they may cause fouling of the membranes and recovery is highly desirable because of their high unit price value. Neutralization is required because the pH requirement of the reverse osmosis membrane. Silica may have to be removed to prevent membrane fouling.

Ammonia Removal

Methods for removal and recovery of ammonia from waste waters are reviewed in Appendix C. The liquid membrane process and ion exchange on clinoptilolite were tested on Stream 1 and the results are included in Appendix C. Neither of these two methods were found attractive. Conventional stream stripping of the ammonia was used for the purpose of cost estimating the total process.

Amines Removal and Recovery: Carbon Adsorption

Nine carbons were evaluated to select the best carbon for the adsorption of the amines. A standard isotherm was run with each carbon using waste water, as received, with no pH adjustment.

Increasing weights of each carbon were added to 100 mls of waste water in bottles that were shaken in a temperature regulated water bath for 24 hours at 25°C. The samples were filtered and analyzed for total organic carbon and an adsorption isotherm was plotted for each carbon.

Figure 2 shows a comparison of the results for three carbons and the results for all the carbons are summarized in Table 3. The carbon with the largest capacity at 1000 mg/l was Westvaco WV-G, 12 x 40 mesh. Subsequently this one was used in the carbon bed tests.

The carbon bed tests were run using four carbon columns operated in series. A variable speed peristaltic pump was used to feed the beds and a three-way solenoid was placed in the line after each column. An electrical timer controlled the solenoids such that after a 19-minute period, the solenoid would open for 15 seconds and divert a 20 ml. sample to a test tube in the SMI model 1205 fraction collector. Each column was sampled sequentially from first to last and the sampling cycle started again. The fraction collector advanced every 18 minutes so that an empty test tube was always ready for the sample. The collected samples were analyzed for total organic carbon. A few samples were also analyzed for the amines by gas chromatography.

Table 4 summarizes the conditions for the bed tests. The first cycle was run at 22 ml/min. (1.06 gpm/sq.ft.) during loading and 44 ml/min. (2.12 gpm/sq.ft.) during regeneration of the carbon. The balance of the cycles were run with these rates reversed. Figure 3 gives the results from the last cycle. The plots for the other three cycles were similar. Table 5 presents a summary of the results.

After the first cycle of loading and regeneration, no further significant change in capacity or TOC recovered was noted.

Further bed tests were run using one large carbon bed. The objective of this test was to provide a large amount of pretreated waste water for the electrodialysis-reverse osmosis tests. The column was 7' x 4" O.D. The carbon bed was 6.5'x 3.5" I.D. The bed volume was 11 liters and the weight of the Westvaco WV-G carbon was 4400 grams.

The regeneration step was followed closely on the third cycle. Figure 4 is a plot of the results. The regeneration stream was divided into three cuts; the first cut included the void volume of the bed and neutralization of the caustic by the acid. This cut was basic and the TOC was that of the original feed. This cut could be recycled to the feed. The second cut was the product cut containing 90 percent of the TOC and was acidic. The TOC concentration was approximately 1.5 percent or approximately 3.0 percent amines. The last cut was low in TOC and high in acid

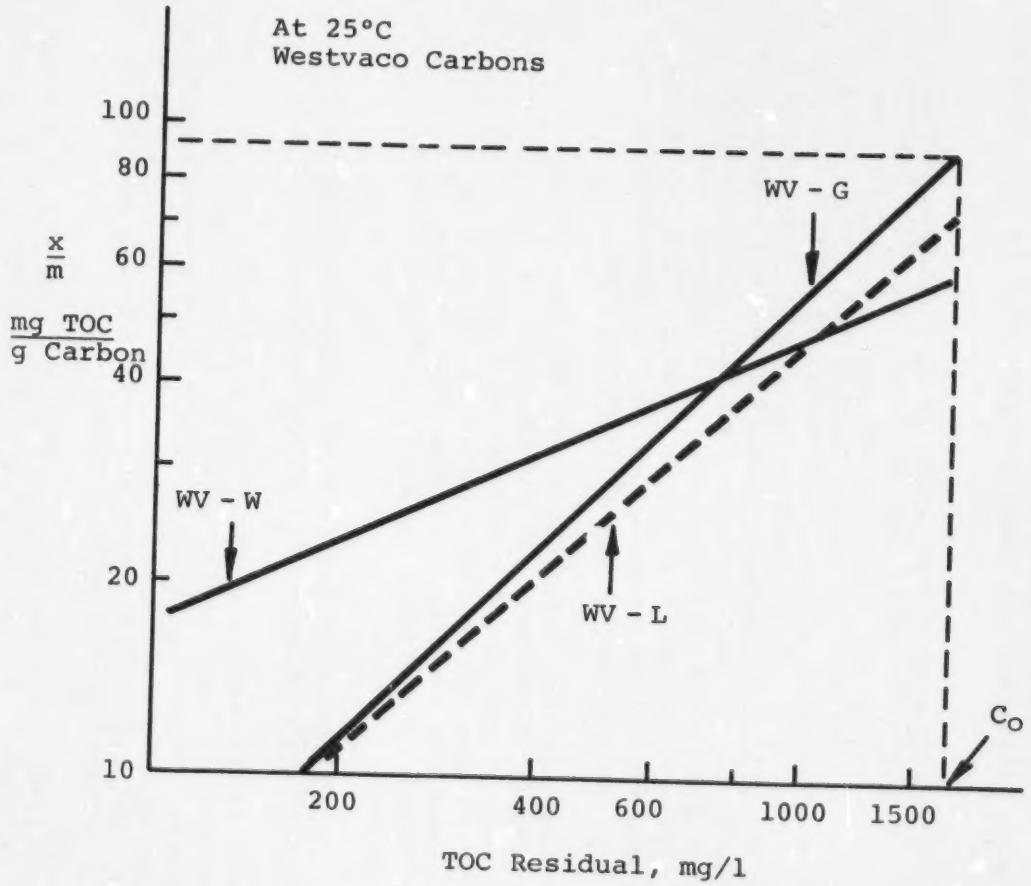

Figure 2. ADSORPTION ISOTHERMS - STREAM 1

Table 3. COMPARISON OF COMMERCIAL ACTIVATED CARBONS FOR AMINES ADSORPTION - STREAM 1
Initial Concentration 1600 mg/l TOC

Activated Carbon	Exhaustion Capacity at 25°C mg TOC/gram carbon
Westvaco WV-G	90
Barneby Chaney SC	84
Westvaco WV-L	72
Hydrodarco 3000	68
Westvaco WV-W	62
Barneby Chaney PC	60
Witco 517	56
Filtrasorb 400	52
Filtrasorb 300	42

Table 4. CARBON BED TEST CONDITIONS - STREAM 1

Feed	Unneutralized Stream 1
Carbon	Westvaco WV-G, 12 x 40 mesh
Columns	(4) 4-1/2 foot x 1 inch i. d.
Bed Volume	(4) x 690 = 2760 mls
Total Bed Height	18 feet
Weight of Carbon	1140 grams
Cross Sectional Area	5.1 sq cm
Temperature	25°C
Pressure	4.5 inch Hg
Regenerant	2N HCl
Regenerant Volume	2 bed volumes

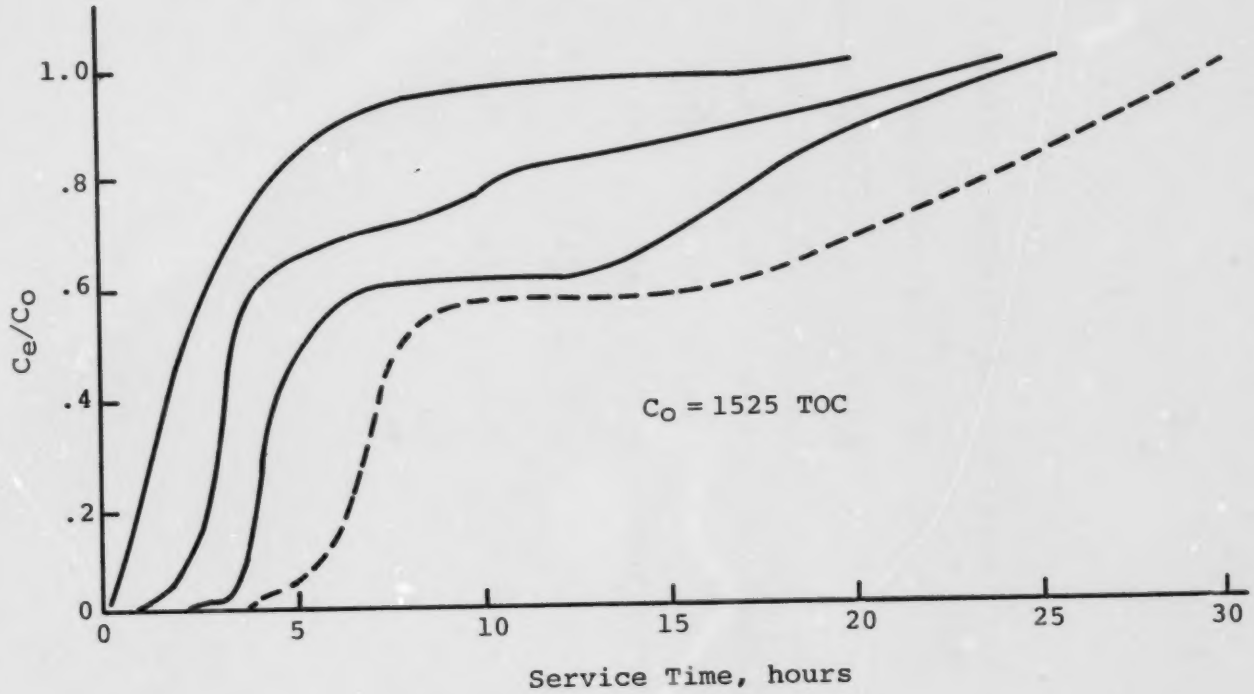

Figure 3. CARBON COLUMN TEST - CYCLE 4

Table 5. CARBON BED TEST RESULTS - STREAM 1

Feed, TOC = 1525 mg/l
Regenerant = 2N HCl - 2 Bed Volumes

	Cycle			
	1	2	3	4
Loading Rate, gpm/sq. ft	1.06	2.12	2.12	2.12
TOC Adsorbed, g	52.9	53.1	49.3	52.7
Capacity, mg TOC/g Carbon	47	47	43	46
Regeneration Rate, gpm/sq. ft.	2.12	1.06	1.06	1.06
TOC Recovered, g	39.1	49.4	48.3	48.5
TOC Recovered, %	74	93	98	93

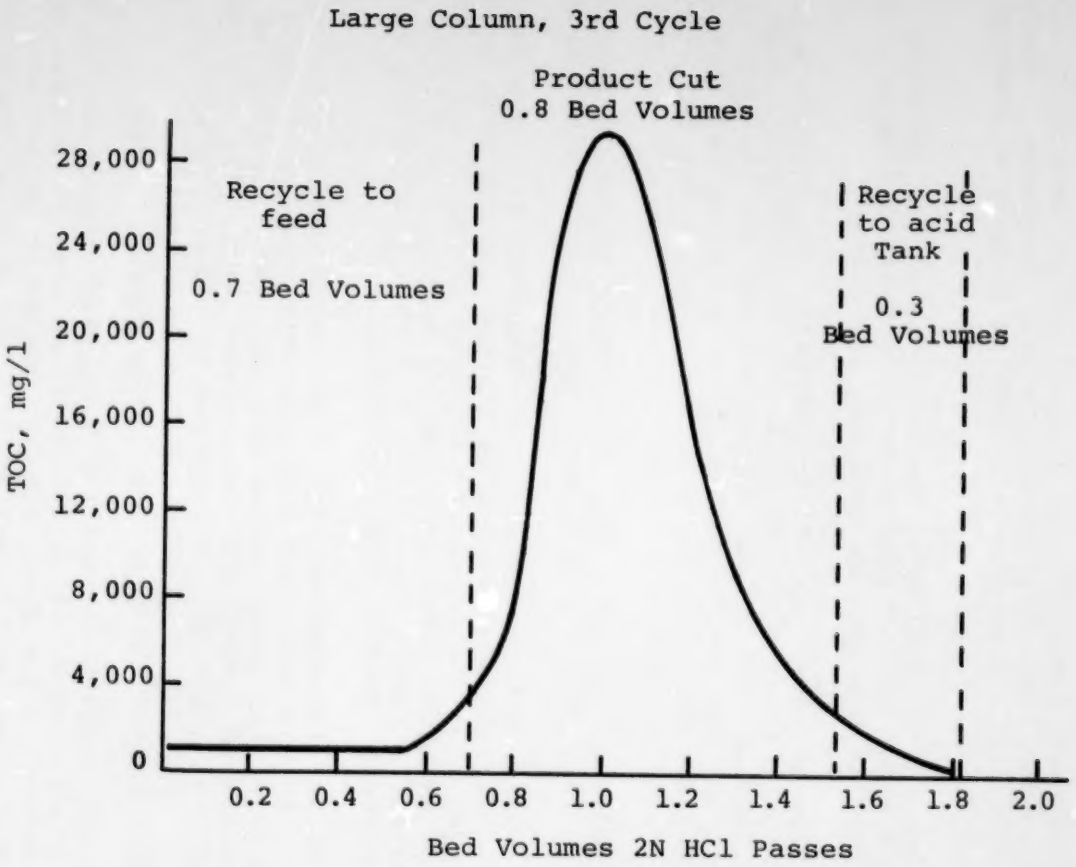

Figure 4. REGENERATION - ACTIVATED CARBON - STREAM 1

and could be recycled to the acid tank. The column was finally washed with a half bed volume of water to flush out the acid before the feed was restarted. The water wash also could be recycled to the acid tank.

Silica Removal

The first electrodialysis-reverse osmosis test using pretreated Stream 1 was terminated shortly after starting because of fouling of the electrodialysis and reverse osmosis membranes. Analysis indicated the fouling substance consisted largely of amorphous silica.

A literature survey indicated the best method for removing silica from water was by adsorption on activated alumina. This was described in a report by Bell, et al, (1968).

An adsorption isotherm was run to determine the equilibrium capacity of the alumina for the silica. Two different mesh ranges of alumina were used. Figure 5 shows the isotherm results. The capacity of the 80-200 mesh alumina was 20 mg. silica/g. alumina, significantly higher than the capacity for the 8-14 mesh.

A column bed test was then run. A small plexiglass column was filled with 129 grams of 30-40 mesh Alcoa F-1 activated alumina.

About 24 liters (190 bed volumes) of synthetic Stream 1 containing 102 mg/l silica was passed through the bed when breakthrough occurred. The breakthrough capacity was 20 mg of silica per gram of alumina. This same alumina was used in a three column set-up to remove the silica from the feed for the electrodialysis-reverse osmosis experimentation.

The alumina was regenerated with 2 bed volumes of 1 N sodium hydroxide. It was indicated qualitatively that the alumina also removed some of the trace amines and that they could be collected in a concentrated fraction during regeneration. The alumina pretreatment will be used as required to remove the silica.

B. REVERSE OSMOSIS AND ELECTRODIALYSIS STUDIES - STREAM 1

The electrodialysis unit used for these experiments was an Asahi Chemical Industries Model SV-5 laboratory electrodialysis unit. Figure 6 describes the SV-5 unit and operating parameters. In the SV-5 unit, the feed is pumped into the dilution recycle tank. The dilution recycle is pumped through the dilution half cells within the electrodialysis stack. There the anions and cations

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Bell, G. R. at al, Office of Saline Water Research and Development. Progress Report No. 286, 1968.

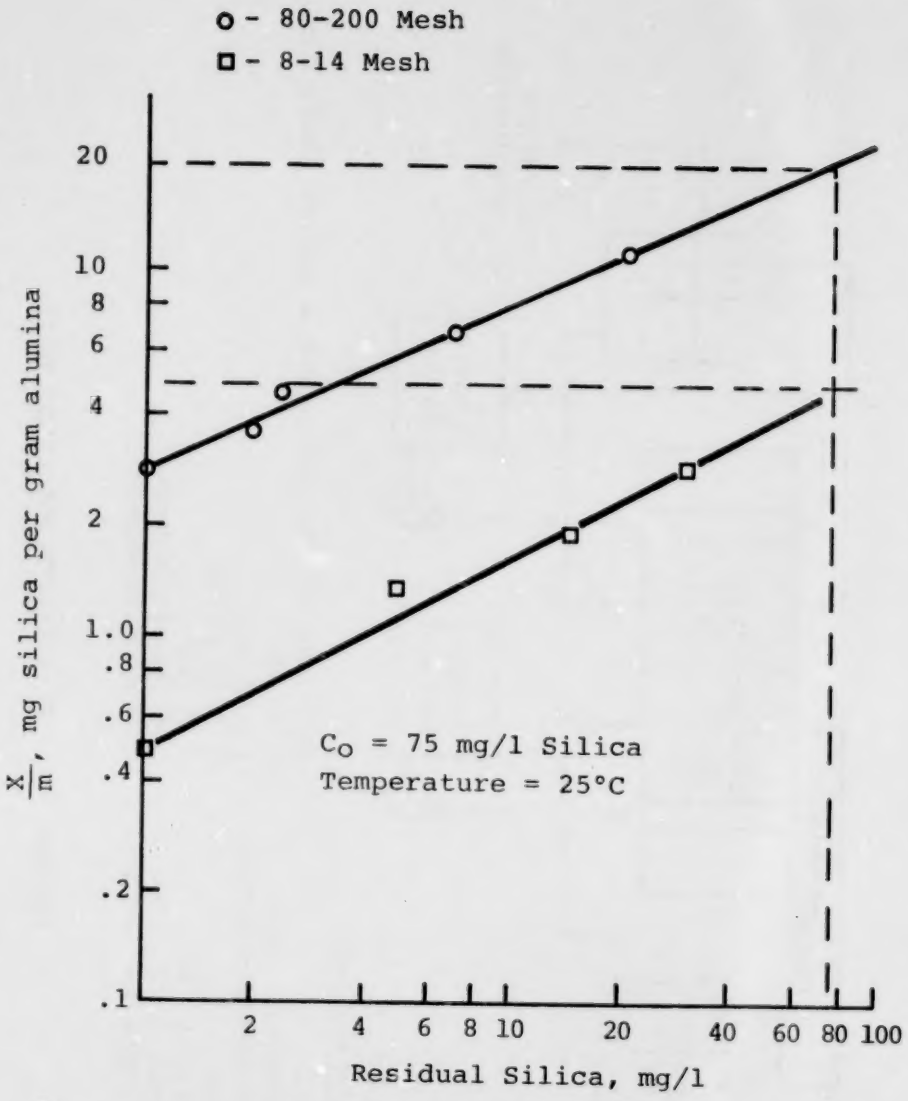
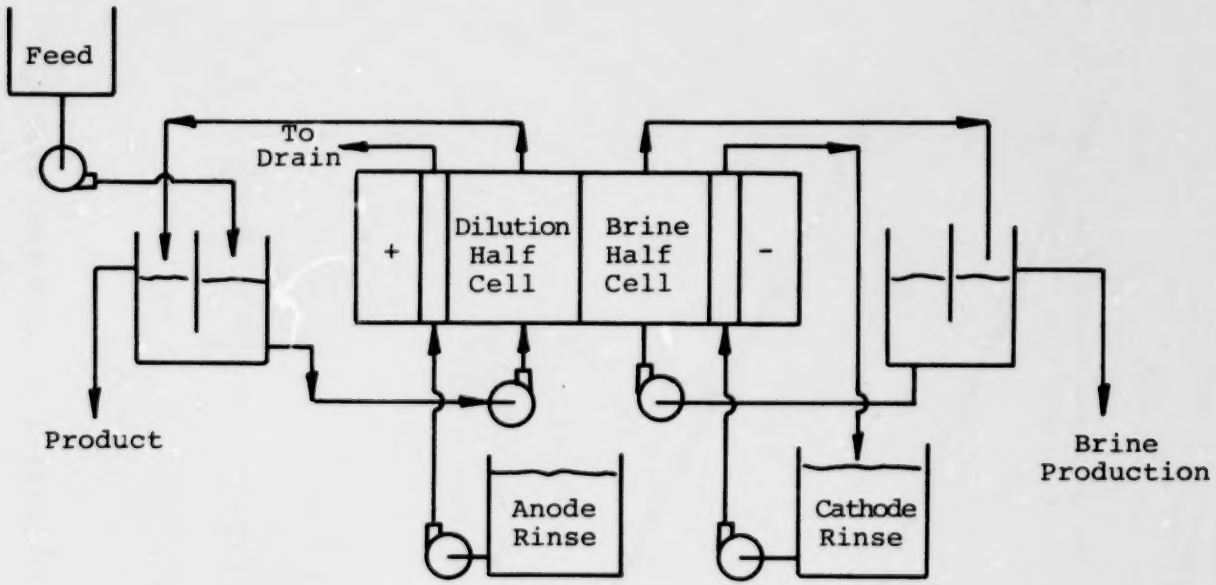


Figure 5. SILICA ADSORPTION ON ACTIVATED ALUMINA



Operating Parameters:

Membranes.	Standard reinforced anion & cation -Asahi Chem.Ind.
Active membrane area .	0.75 dm^2
Linear velocity-dilution .	15 cm/sec
Stack size	5 cell pairs
Brine recycle rate	0.3 gpm
Anode rinse flow rate. . .	100 ml/min/amp-dm^2
Cathode rinse flow rate. .	100 ml/min/amp-dm^2

Figure 6. SV-5 ELECTRODIALYSIS UNIT

are transported to the adjacent brine half cell compartments under the influence of the direct current potential generated by the anode and cathode. The depleted dilution recycle then returns to the tank. The brine flow is recycled and the increase in volume caused by the transport of water and brine from the dilution compartment is bled off as the brine production. The depleted product water is bled off the dilution recycle tank. The cathode is rinsed with HCl to remove the hydrogen gas and caustic that is produced at the cathode. This stream is recycled and replaced when depleted. The anode is rinsed with NaCl to sweep out the chlorine and acid produced at the anode. This stream is not recycled to prevent deterioration of the end membrane from chlorine exposure.

A Universal Water Corporation laboratory model reverse osmosis unit designed for [small flat] membranes was modified for the use of Dow hollow fine fiber reverse osmosis cartridges. The cartridge used was a low pressure Dowex XFS-4167.07 Permeator with a nominal capacity of 250 GPD. Figure 7 describes the equipment.

Electrodialysis Preliminary Evaluation

Stream 1, neutralized to pH 7, but untreated with carbon adsorption was used as feed to determine the extent of the problems encountered with the electrodialysis equipment. The potential across the stack was held at 3 volts and the current density was allowed to vary.

The experiment was run for 12 hours with the brine reaching a concentration of 10.4 percent NaCl. The dilution stream was replaced with more feed and the run continued for 12 more hours. The final concentration was 12.8 percent NaCl (Figure 8). The organics were concentrated in the brine stream. The TOC was concentrated from 1235 mg/l in the feed to 5,144 mg/l in the brine and only 185 mg/l in the dilution stream. The organic nitrogen of 1180 mg/l in the feed was concentrated to 5,100 mg/l in the brine and only 112 mg/l in the dilution stream. The stack was dismantled and the cation membranes were found to be fouled. Analysis of the dilution and brine streams indicated that the amines were being transported. However, the heavier amines must have been trapped in the membranes. Attempts to regenerate the membranes by soaking in caustic failed.

The electrodialysis apparatus was then tested on a pretreated Stream 1 feed with a composition shown in Table 6. The dilution and brine recycle tanks were filled with 2 liters of feed and then the unit was operated until equilibrium was reached, in 10 hours. No additional feed was added. Figure 9 shows the results of the test. A concentration of 15.5 percent NaCl was considered to be satisfactory level.

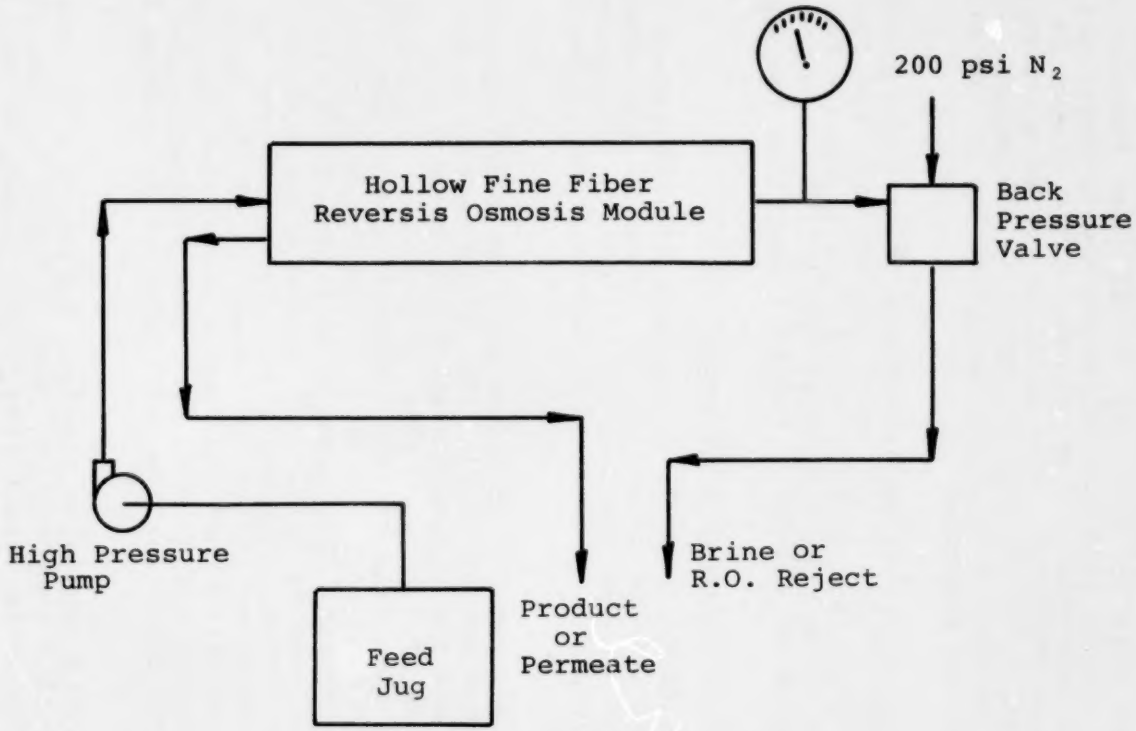


Figure 7. REVERSE OSMOSIS EQUIPMENT

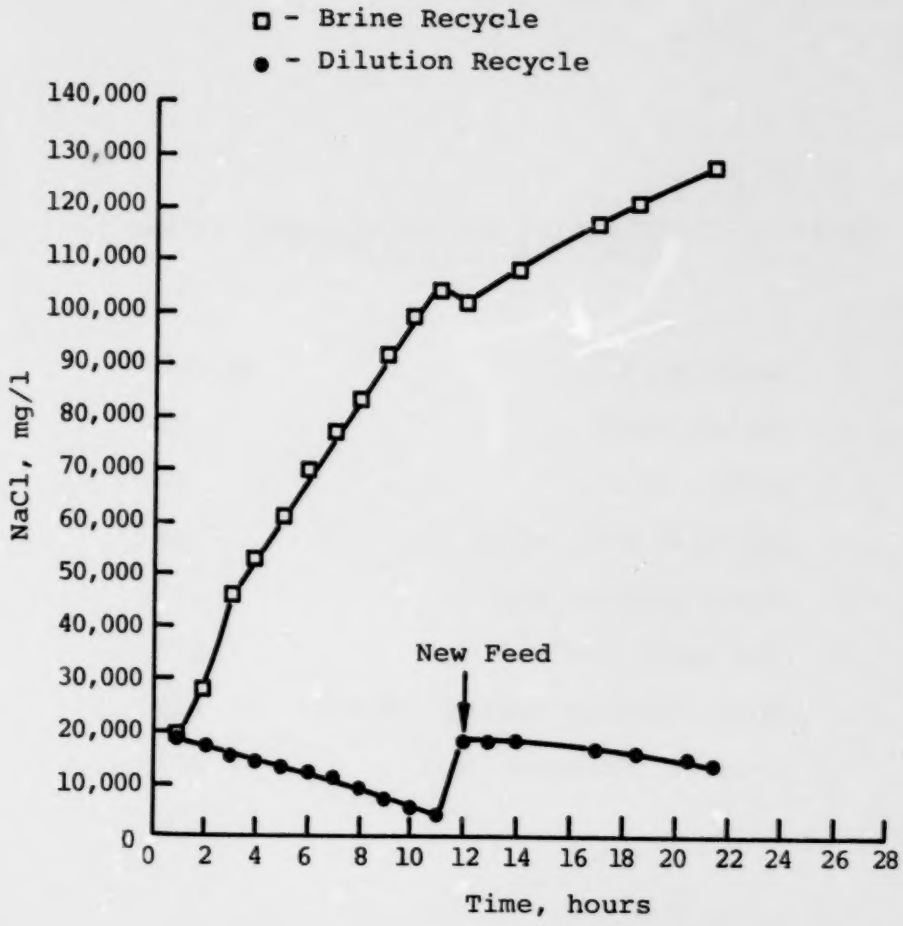


Figure 8. ELECTRODIALYSIS OF NEUTRALIZED UNTREATED STREAM 1

Table 6. PRETREATED AND NEUTRALIZED STREAM 1 WASTE WATER COMPOSITION

pH	7
NaCl, mg/l	14,750
$CaCl_2$, mg/l	59
$MgCl_2$, mg/l	33
NH_3-Nitrogen, mg/l	134
Total Carbon, mg/l	170
Inorganic Carbon, mg/l	13
Total Organic Carbon, mg/l	159
Organic Nitrogen, mg/l	107

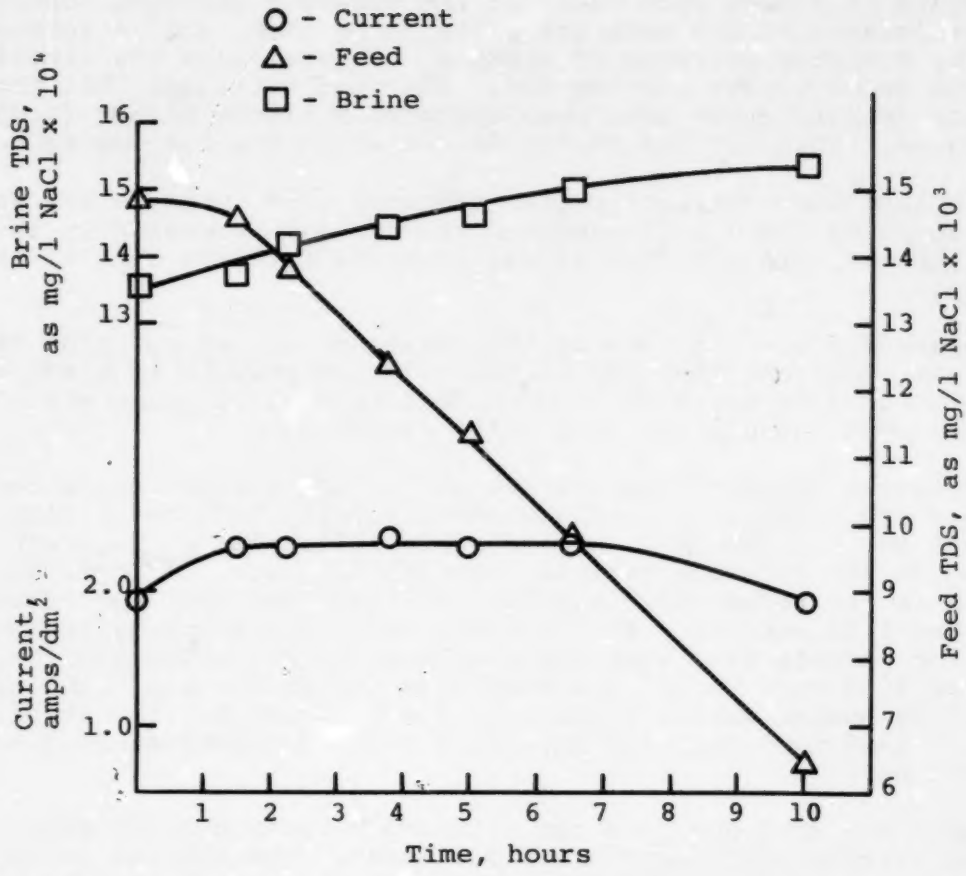


Figure 9. ELECTRODIALYSIS OF PRETREATED STREAM 1

As the current density, measured in amperes per square decimeter (amp/sq.dm.), is increased through the system of membranes and solutions, the rate of electrical transport increases. A current density will be reached at which the concentrations of the electrolytes at the membrane interfaces on the depleting sides will approach zero. At this density, usually called the limiting current density, H^+ and OH^- ions from the ionization of water will begin to be transferred through the membranes. The presence of layers of almost pure water at the membrane surfaces causes the resistance of the membrane cells to be high, and is accompanied by a higher increase of voltage. Figure 10 is the limiting current density plot for the run. The plot indicates that the current density could have been operated a little higher (2.75 amp/sq.dm.) than the 2.4 amp/sq.dm. at which the run was made.

To simulate the operation of the combined ED-RO unit, a run was made in which the dilution stream from ED was processed in the RO unit, then the reject from RO was combined with the feed to the ED unit.

The operation was the same as the previous run, except that the feed was added continuously to the dilution recycle tank and the dilution product was bled off. A small amount of brine was also removed continuously from the brine recycle.

The dilution recycle flow was set at 0.5 GPM and the brine recycle was 0.3 GPM. The stack voltage was 3.0 volts and the initial current was 1.8 amp/dm^2. At the start, 2500 mls. of feed was placed in the dilution recycle tank and 1300 mls. of feed was placed in the brine recycle tank. Initial feed NaCl concentration was 1.41 percent. The feed was added continuously to the dilution recycle tank when the dilution recycle concentration reached 4000 mg/l NaCl. The feed rate was 18 mls/min. The run lasted 9½ hours, during which time the dilution recycle stabilized at 2400 mg/l NaCl and the brine recycle increased to 8.6 percent NaCl.

The unit was shut down and the dilution recycle was transferred to the reverse osmosis unit and processed. The reverse osmosis reject concentration was 6760 mg/l NaCl, which was mixed with more electrodialysis feed and placed back in the electrodialysis unit. The dilution recycle was now 1.067 percent NaCl. The unit was restarted with the same brine recycle. When the dilution recycle reached the 4000 mg/l NaCl concentration, the feed was started at 27 ml/min. The results of the runs are plotted in Figures 11 and 12. The second run continued for 5 hours, during which the dilution recycle stabilized at approximately 4000 mg/l NaCl. The brine recycle reached 12.3 percent NaCl. The maximum current density allowable was 2.18 amp/dm^2 as indicated in the limiting current density plot in Figure 13. No operational problems were encountered during the experiment. Analyses of grab samples during the run indicated the total organic carbon

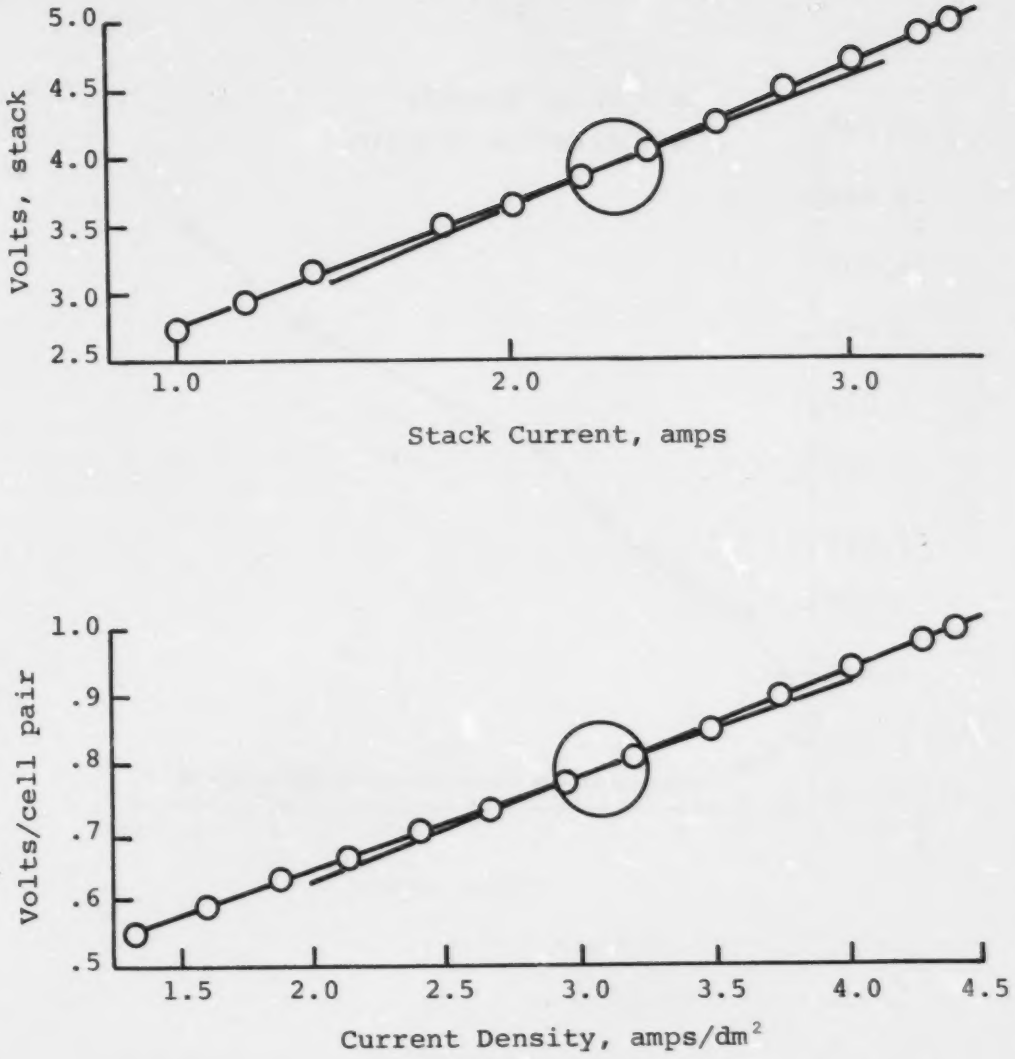


Figure 10. ELECTRODIALYSIS OF PRETREATED STREAM 1 - LIMITING CURRENT DENSITY

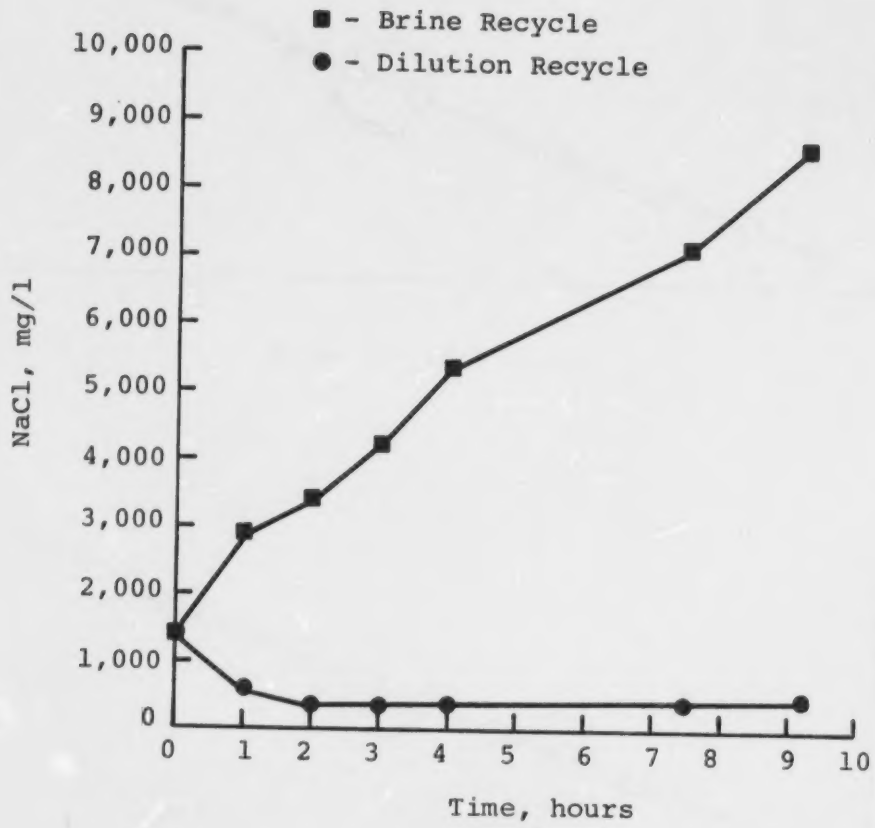


Figure 11. CONTINUOUS ELECTRODIALYSIS OF PRETREATED STREAM 1 FEED

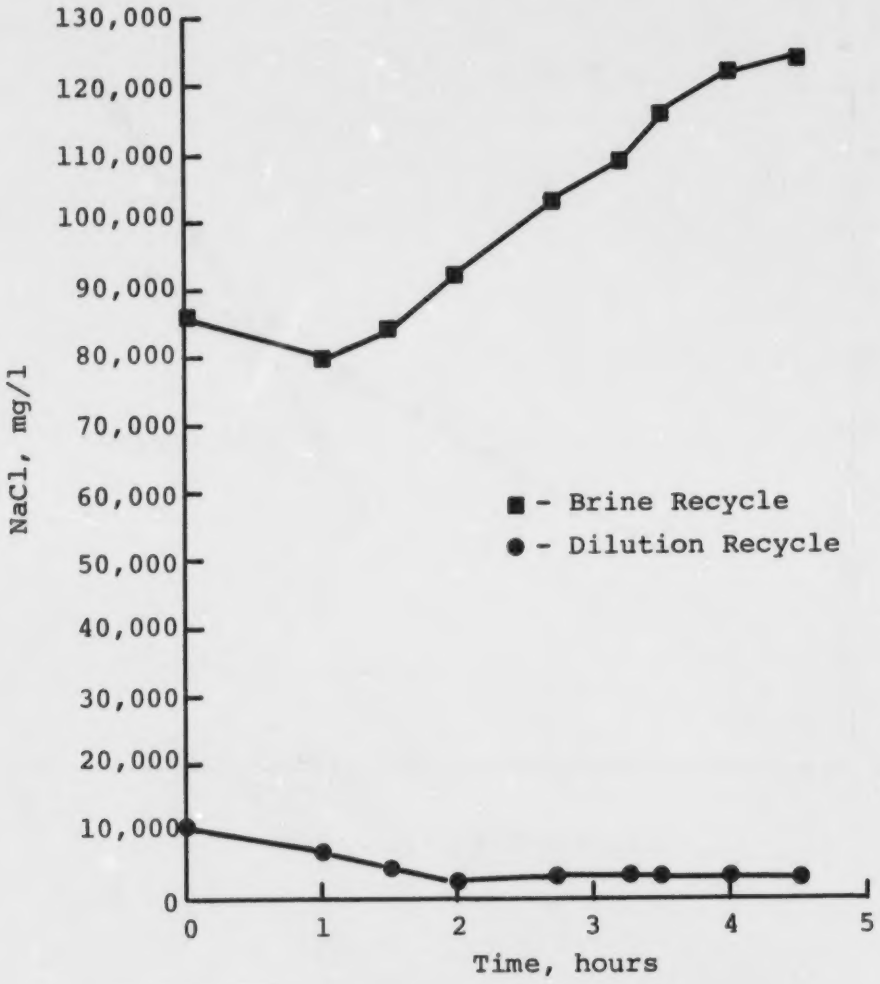


Figure 12. CONTINUOUS ELECTRODIALYSIS OF PRETREATED STREAM 1 PLUS RO REJECT MIXTURE

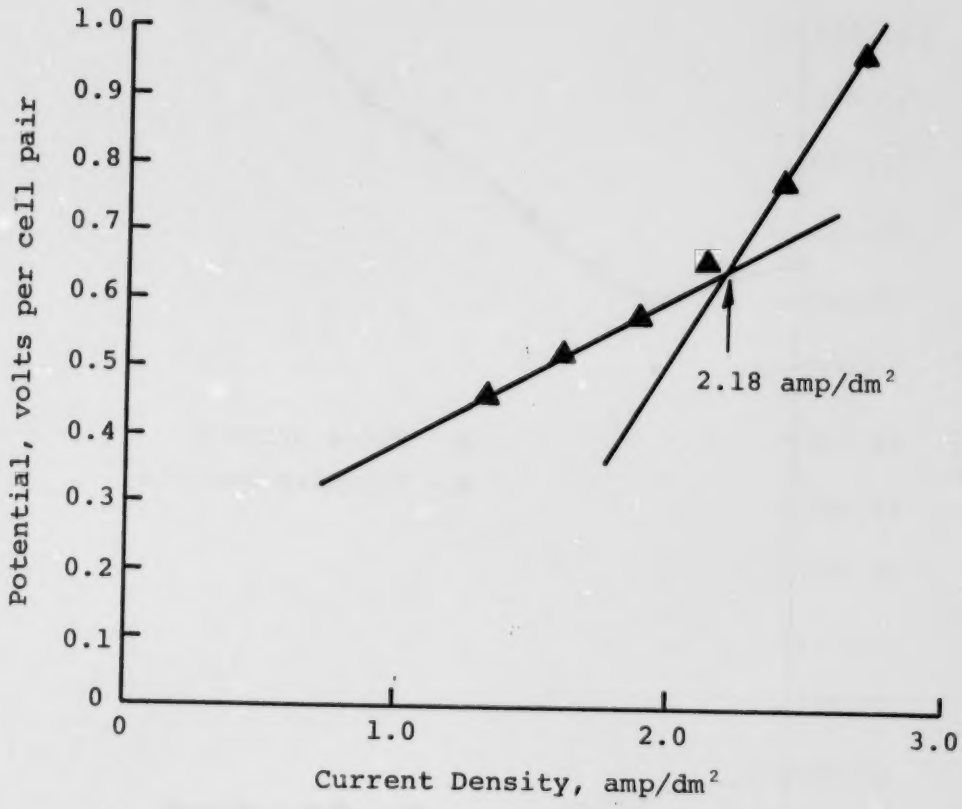


Figure 13. LIMITING CURRENT DENSITY OF COMBINED PRETREATED STREAM 1 AND RO REJECT STREAM

and the ammonia nitrogen was transported and concentrated in the brine. The reverse osmosis membrane also rejected the TOC and the ammonia nitrogen.

Reverse Osmosis Tests

The electrodialysis dilution recycle is feed for the reverse osmosis unit in the total recycle system concept. Several experiments were made in connection with the electrodialysis evaluation experiments. The objectives of these experiments were to determine operating conditions for the reverse osmosis unit to produce less than 500 mg/l NaCl product at 200 psi, and test for the possibility of membrane fouling. The results of the runs are summarized in Table 7. The results indicate that: Satisfactory quality product water can be produced from the reverse osmosis unit from 4000 mg/l NaCl feed at 200 psi and a 50-50 product-reject split. The ammonia-nitrogen, TOC and organic-nitrogen are all concentrated in the reverse osmosis reject, and no fouling of the membrane was indicated.

Evaluation of Combined Electrodialysis-Reverse Osmosis Treatment of Stream 1

The objective of this experiment was to combine the previously evaluated electrodialysis and reverse osmosis units and to operate the combined units continuously on pretreated neutralized Stream 1 to determine the necessary design parameters.

A schematic of the combined laboratory units is given in Figure 14. Neutralized pretreated Stream 1 [1] is mixed with the reject [6] from the reverse osmosis unit. This stream [2] is fed into the dilution recycle loop. A portion of this stream [4] is fed to the reverse osmosis unit. It is expected that this stream will have a concentration of 4000 mg/l NaCl. Because the electrodialysis unit was not well matched to the reverse osmosis unit in flow capacity, a large portion of the reverse osmosis product [7] and the reject [8] was recycled and mixed with the dilution recycle [4] to form the reverse osmosis feed [9]. A portion of the product flow [5] is taken off continuously. A portion of the brine recycle is taken off as brine product [3]. The feed flow [1] should be exactly equal to the sum of the brine [3] and the reverse osmosis product [5].

Prior to the run, a standard brine with a sodium chloride concentration of 14,000 mg/l was run under the same conditions as the actual run. The feed rate was 32 ml/min. The brine production rate was 3 mls/min. The reverse osmosis product rate was 29 ml/min. The dilution stream NaCl concentration was 4000 mg/l. The reverse osmosis reject NaCl concentration was 7900 mg/l. The reverse osmosis product contained 640 mg/l NaCl. The reverse osmosis split was 50 percent product-50 percent reject. The NaCl rejection was 98.8 percent. The operating current density was

Table 7. REVERSE OSMOSIS EVALUATION

Electrodialysis Dilution Recycle Feed
200 psi

	Run*		
	1	2	
NaCl, mg/l	4030	4210	3770
Feed Flow, ml/min.	704	834	709
Product NaCl, mg/l	486	476	503
Product Flow, ml/min.	356	404	353
Reject NaCl, mg/l	7510	7411	6760
Reject Flow, ml/min.	348	430	356
Split	51 - 49	48 - 52	50 - 50

*Run 1 - E.D. Recycle from Pretreated Stream 1.
Run 2 - E.D. Recycle, Stream 1.
Run 3 - E.D. Recycle from Continuous Run.

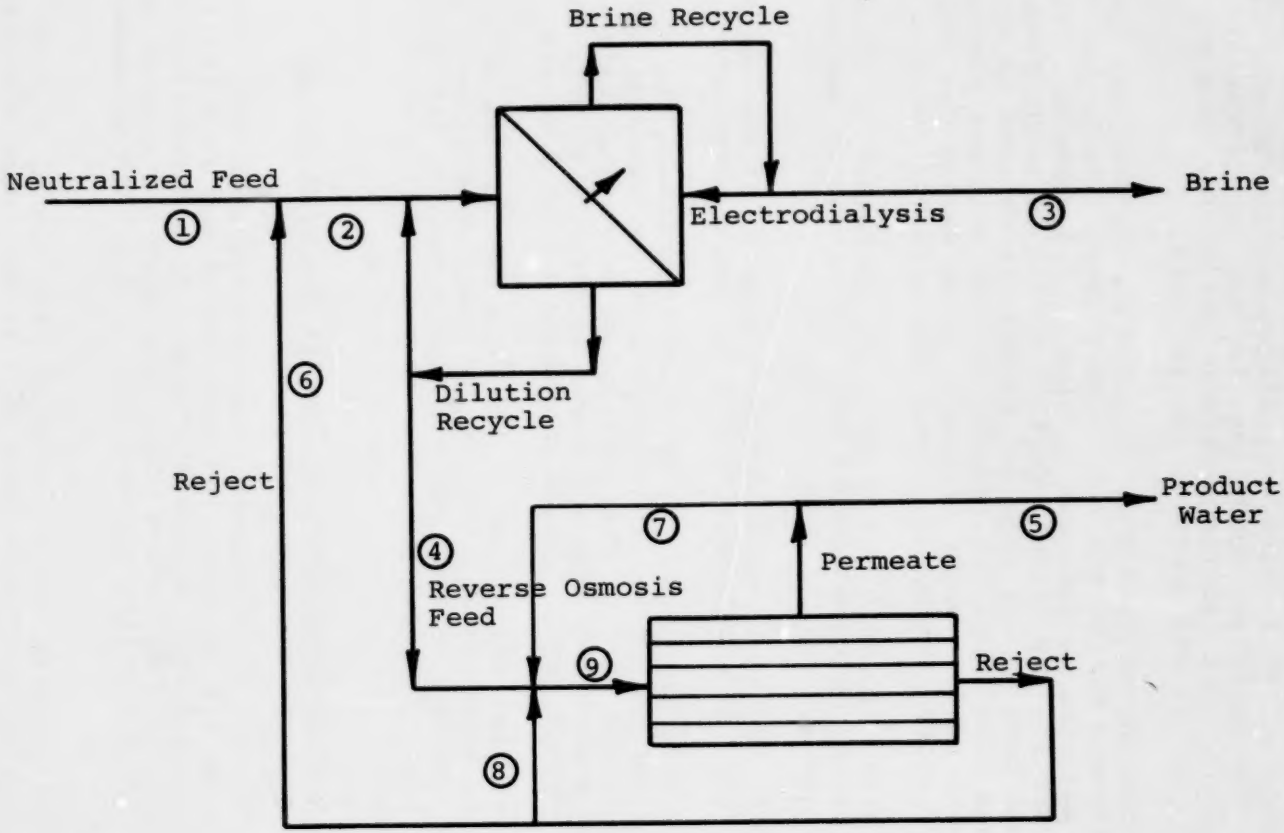


Figure 14. ED - RO INTEGRATED SYSTEM
TREATMENT OF STREAM 1

3.2 amps/dm^2. The limiting current density was found to be 3.5 amps/dm^2. No operational difficulties were noted.

This run was terminated and the feed was switched to the neutralized pretreated Stream 1, with composition similar to that given in Table 6. The operating conditions for the experiment are shown in Table 8. The limiting current density for this run was 1.8 amps/dm^2, and it was operated for 20 hours.

Figure 15 shows the changes that occurred in the critical operating parameters during the run. The current density had to be continually adjusted to maintain a value of 2.4 amps/dm^2. As is noted in Figure 15, the current density continued to decrease. The adjustment back to 2.4 amps/dm^2 caused the voltage to increase. While this was occurring, the reverse osmosis unit was plagued with decreasing product water recovery. Also during the run, the dilution NaCl concentration increased from 4000 mg/l to 6700 mg/l.

The brine started at 146,000 mg/l NaCl and decreased to 136,000 mg/l. The reverse osmosis product NaCl concentration increased from 500 mg/l to 815 mg/l.

After 20 hours, the units were shut down because of the operational problems, and the electrodialysis stack was dismantled.

A thick, oily film was found on the anion membranes. The material was collected for analysis. The analysis of the material indicated that it was 16.8 percent silicon or 36 percent silicon dioxide. The pretreated feed was found to contain 69 mg/l silica. The reverse osmosis reject stream contained 130 mg/l silica.

It was apparent that the silica in the feed was fouling both the electrodialysis membrane and the reverse osmosis membrane. Also the operating current density was much lower than it was during the standard run. The feed will also have to be treated to remove silica.

Continuous Electrodialysis-Reverse Osmosis Run with Silica Removed

Neutralized carbon treated Stream 1 was treated with activated alumina to remove the silica. The analysis of the feed was the same as the previous run, except that the silica concentration was now 10 mg/l. The operating conditions were the same as the previous run. The limiting current density for this solution was 1.7 amps/dm^2.

For a feed rate of 28 mg/min., a product from the RO unit of 21 ml/min. and a brine product rate of 3 ml/min. were obtained. The reject of RO was 8700 mg/l NaCl and the product was 400 mg/l NaCl. The brine concentration of 14 percent NaCl was ten times the concentration of the feed. The ED unit was operated at 0.74

Table 8. ELECTRODIALYSIS - REVERSE OSMOSIS COMBINED TEST, STREAM 1

Electrodialysis Unit:	
Membranes	- A&K 101 Asahi Chemical Ind.
Stack Amps	- 1.6
Stack Volts	- 7.3
Cell Pairs	- 10
Feed Flow	- 30 ml/min.
Dilution Flow	- 1.7 l/min.
Dilution NaCl	- 4000 mg/l
Dilution pH	- 7.1
Dilution Temperature	- 26°C
Brine Production	- ∿3 mls/min.
Reverse Osmosis Unit:	
R.O. Membrane	- Dowex XFS-4167.07 Permeator
Pressure	- 200 psi
Feed Rate	- 640 ml/min.
Product Recycle Rate	- 317 ml/min.
Reject Recycle Rate	- 324 ml/min.
Split	- 50 - 50
Product Rate	-27 ml/min.

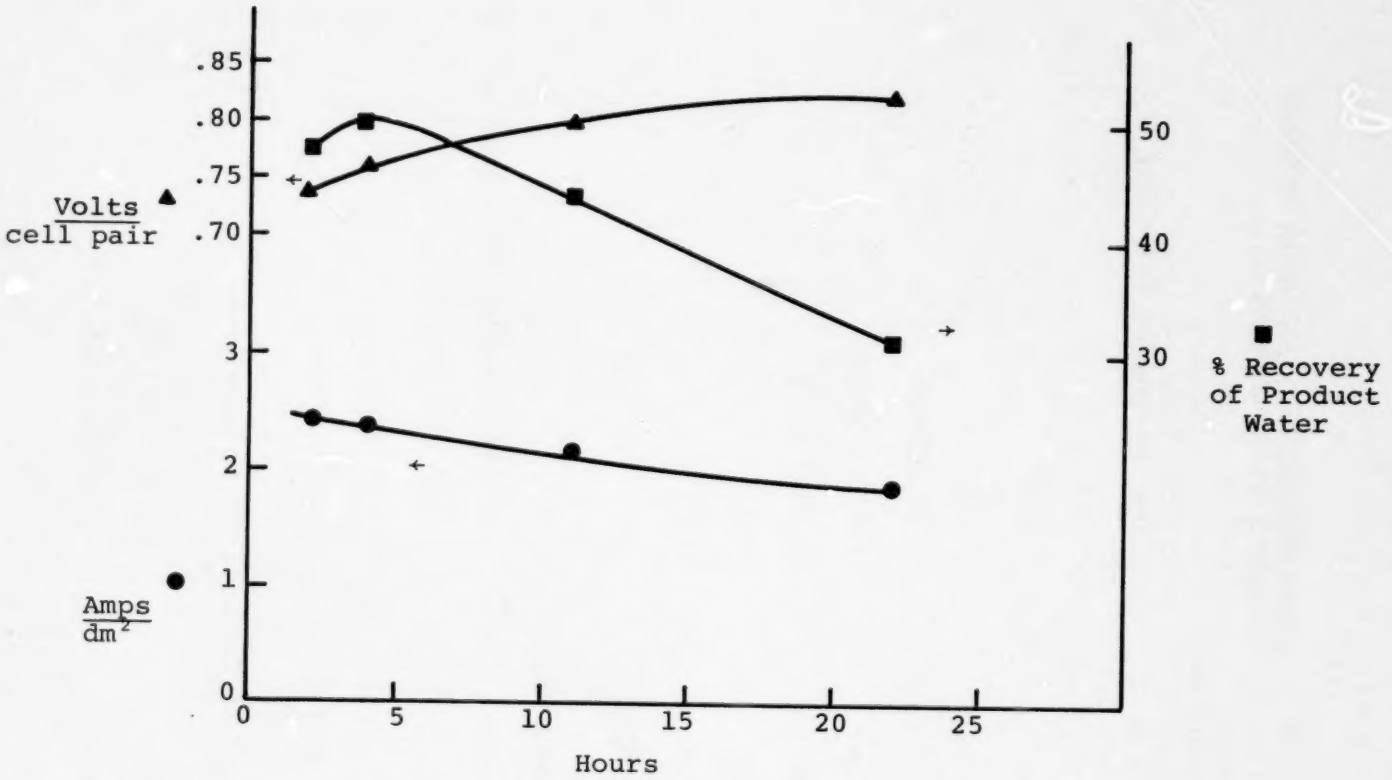


Figure 15. ED-RO COMBINED OPERATION - CRITICAL PARAMETERS - STREAM 1 WITHOUT SILICA REMOVAL

volts per cell pair and a current density of 1.6 amps/dm^2. Figure 16 plots the same critical operational parameter as shown in the previous experiment. The experiment was run for 70 hours with no operational difficulties.

The current density remained stable throughout all of the experiment. The reverse osmosis recovery increased somewhat toward the end of the run. Of greatest interest is the fact that the operating current density was still much lower than that during the standard run. The probable cause is the low level of amines present in the feed. This emphasizes the need for near complete removal of these compounds.

C. TOTAL RECYCLE SYSTEM DESIGN AND COST ESTIMATE

A flow diagram of the total recycle system of Stream 1 is given in Figure 17, which includes a material balance and flow rates of each stream. The ammonia removal step is not shown on the flow sheet, and if required, its design is based on conventional steam stripping.

A summary of the estimated capital and operating costs of the total system is given in Table 9.

Details of the design and cost estimates of the unit operations required for the total recycle of Stream 1 are shown in Appendix D.

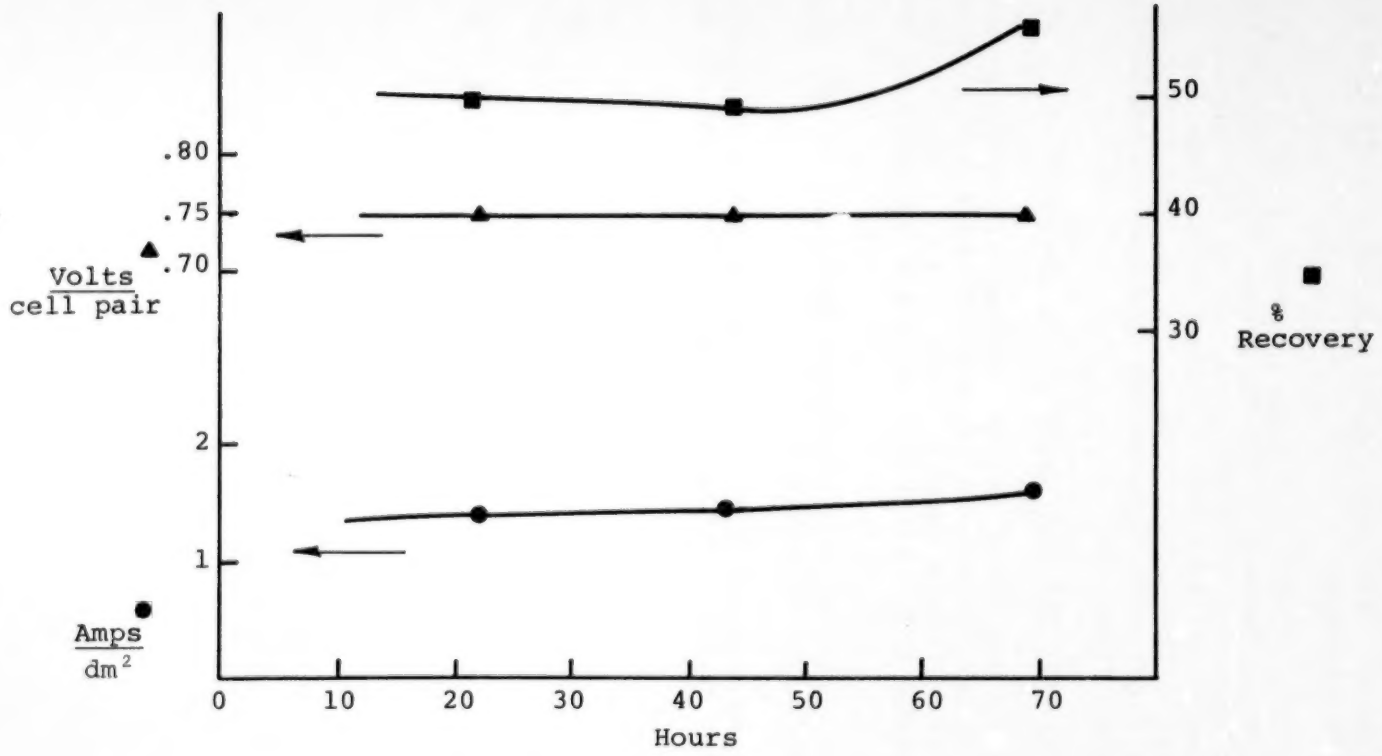
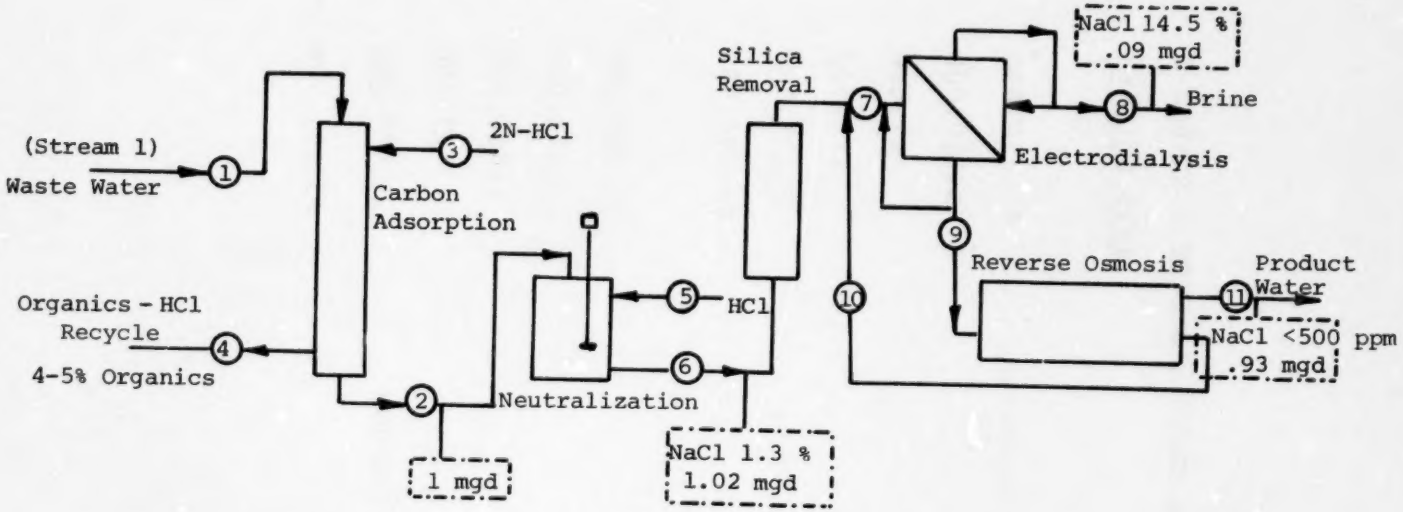


Figure 16. ED - RO COMBINED OPERATION-CRITICAL PARAMETERS - STREAM-1, WITH SILICA REMOVAL



lb./hr.	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩	⑪
TOC	600	630	2	568	--	30	30	544	--	--	--
NaOH	3,000	3,000	--	--	--	--	--	--	--	--	--
Silica	21	21	--	--	--	21	4	72	--	--	--
HCl	--	--	9,800	--	3,000	--	--	--	--	--	--
NaCl	300	3,100	--	--	--	5,900	8,720	5,700	3,020	3,870	150
H_2O	343,600	402,940	162,600	70,900	1,108	417,899	720,000	34,000	678,000	294,000	384,000
Total	374,521	409,721	172,400	71,466	8,108	423,850	720,720	39,700	681,020	296,870	384,150

Figure 17. TOTAL RECYCLE SYSTEM - STREAM 1
FLOW DIAGRAM AND MATERIAL BALANCE

Table 9. COST FOR TOTAL RECYCLE SYSTEM - STREAM 1

	1975 Dollars
Capital Cost:	
Ammonia Removal (Steam Stripping)	$1,156,000
Carbon Adsorption	2,330,000
Neutralization	87,000
Silica Removal	261,000
Electrodialysis-Reverse Omosis	3,115,550
Total	$6,949,550
Operating Cost:	
Ammonia Removal	$ 300,000
Carbon Adsorption	2,358,000
Neutralization	1,900,000
Silica Removal	87,400
Electrodialysis-Reverse Osmosis	646,300
Total	$5,291,700 $/yr

SECTION 6

STREAM 2. TOTAL RECYCLE SYSTEM

Stream 2 contains 4.2 percent total dissolved solids. It was selected to study the electrodialysis-reverse osmosis total recycle, as it represents the highest concentration that can possibly be treated with such a system.

A. PRETREATMENT STUDIES

The characterization of Stream 2 indicated that at least two steps would be necessary before the waste water could be treated by the electrodialysis-reverse osmosis process. These steps are aluminate removal and recovery (neutralization) and organic carbon removal.

Aluminate Removal-Neutralization

The neutralization of Stream 2 caused the precipitation of the aluminate ion in the form of aluminum hydroxide. Precipitation starts at a pH of 11.2. Analysis of the supernatant after adjustment to pH 7.0 indicated less than 1 mg/l of aluminun ion present. Therefore virtually all the aluminate is removed at pH 7. The characterization indicated that Stream 2 had an average alkalinity of 4950 mg/l as sodium hydroxide, a 0.124 N sodium hydroxide solution. Therefore 0.124 equivalents of hydrochloric acid per liter would be required for neutralization or 10.3 gallons of concentrated HCl (12 N) per 1000 gallons of Stream 2.

The suspended solids formed during neutralization must be removed and concentrated. The concentrated aluminum hydroxide may then be converted to aluminum chloride for reuse in the process or sold as a coagulant. The average suspended solids formed during neutralization of Stream 2 is 1500 mg/l.

Gravity settling tests were run on the sludge to determine the design parameters for a gravity settler. Varying concentrations of sludge were placed in one liter graduated cylinders. A 4 rph stirrer was placed in each cylinder and the interface level was recorded at various time intervals. The sludge settles very poorly. Addition of varying concentrations of Purifloc A-23 flocculant to the sludge in a standard jar settling test produced no improvement in settling rate or decrease in sludge volume. The range of flocculant concentration was from 0.3 to 25 mg/l of A-23. The addition of up to 200 mg/l of ferric chloride also had no significant effect on the settling.

Figure 18 is a plot of the settling velocity versus initial solids concentration for the gravity settling tests. Figure 19 is a plot of solids flux versus solids concentration. From this graph using the Yoshioka method as described by Vesilind (1974), the minimum solids flux can be determined for any desired under flow concentration and the surface area for the settler can be determined if the daily flow is known. Table 10 presents the design solids flux and settler surface area for various underflow sludge concentrations. The design flow was 1 MGD, the initial solids concentration was 1500 mg/l. This information will be used to design a gravity settler for Stream 2.

A comparison was made of various granular activated carbons to determine which has the greatest capacity for the organics (Mainly benzene) in Stream 2. This was done by adding 0.05 grams of each carbon and mixing with 250 mg/l of neutralized Stream 2. The carbon with the greatest capacity was selected for further evaluation. The results are shown in Table 11. The best carbon was Witco 517.

An adsorption isotherm was run at 25°C with Witco 517. A synthetic Stream 2 sample was used. Figure 20 presents the isotherm obtained. Equilibrium capacity was determined to be 160 mg of TOC per gram of carbon.

A carbon bed test was run using actual Stream 2 waste water. A 1-in. I.D. glass column was filled with 175 grams of prewashed Witco 517 to a height of 2.3 feet. The bed volume was 690 mls. The feed rate to the column was 42 mls/min or 2.0 gpm/ft^2. Stream 2 waste water was neutralized, settled and the decant was fed to the column. The effluent from the column was analyzed periodically for benzene and TOC. The benzene concentration of the feed was below average for the waste because benzene was lost to the air during the neutralization and settling step. Figure 21 is a plot of the breakthrough curve. Breakthrough was achieved at 330 hours of operation and exhaustion took place at 370 hours. The average feed benzene concentration was 29 mg/l. The breakthrough capacity was 134 mg benzene per gram of carbon. The exhaustion capacity was 147 mg benzene per gram carbon which is higher than the isotherm capacity of approximately 100 mg of benzene per gram of carbon.

The average TOC of the feed during the test was 60 mg/l and the average TOC of the effluent was 18 mg/l. There is apparently a small amount of TOC which will not adsorb on the carbon. A carbon bed will be designed to treat Stream 2 before electrodialysis-reverse osmosis treatment using this data. Regeneration of the carbon will be done thermally.

Vesilind, P. A. Treatment and Disposal of Wastewater Sludge, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 1974.

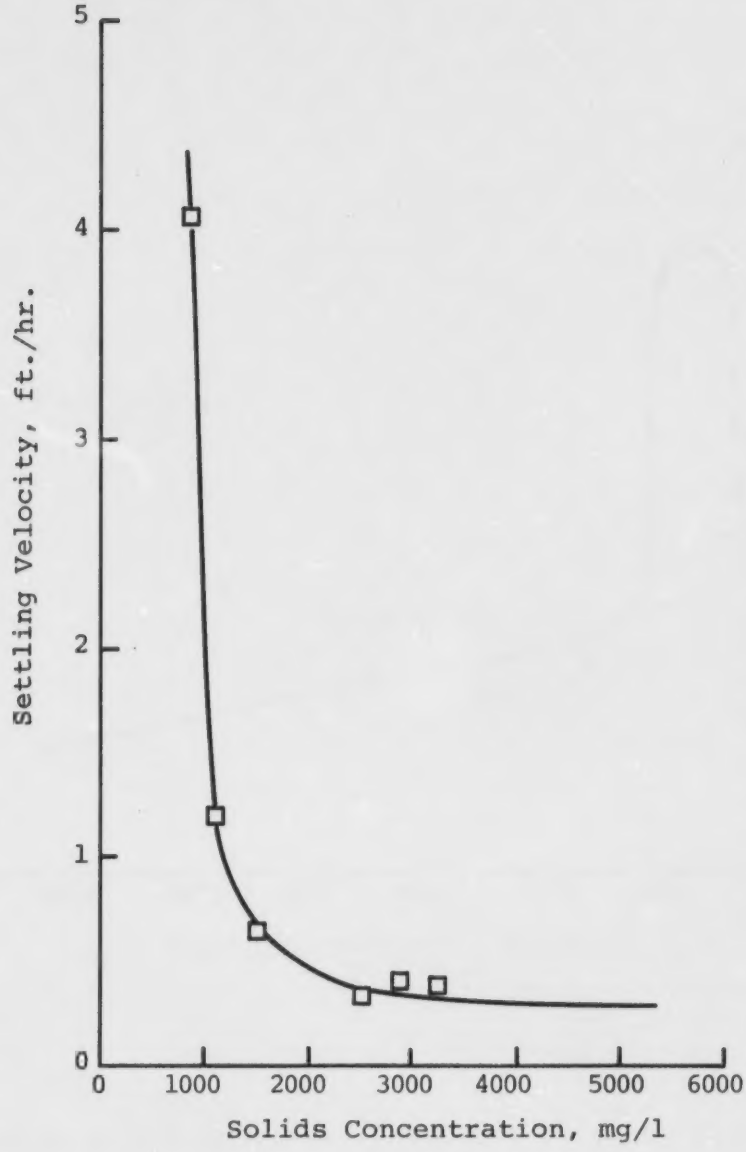


Figure 18. GRAVITY SETTLING - ALUMINUM HYDROXIDE SLUDGE - STREAM 2

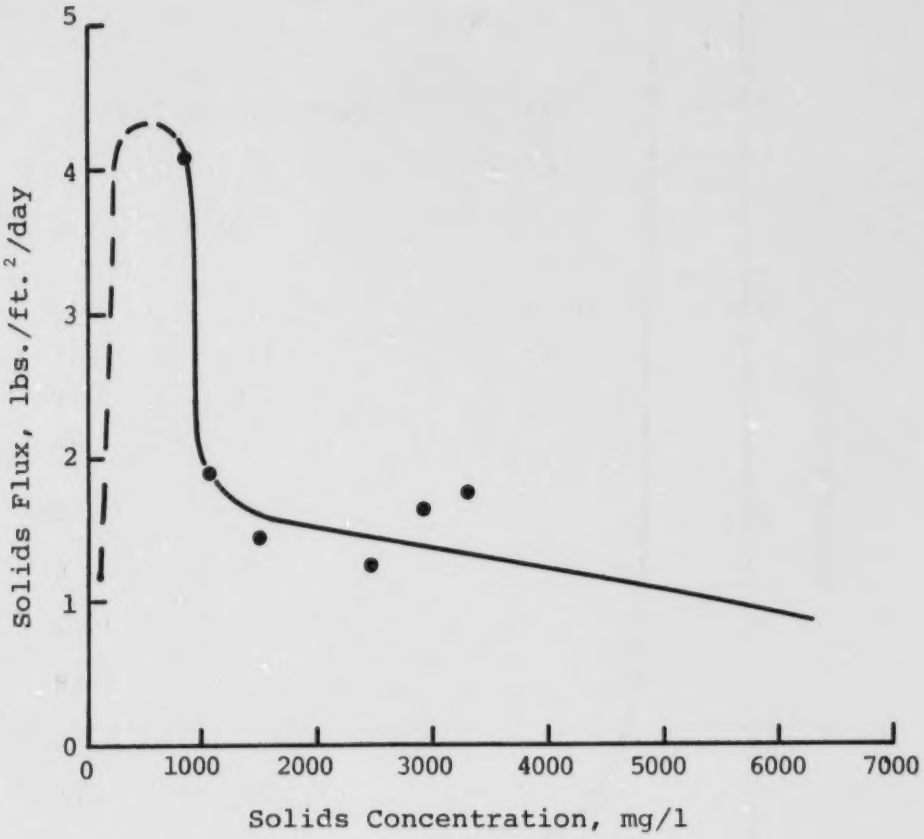


Figure 19. GRAVITY SETTLING - ALUMINUM SOLIDS FLUX - STREAM 2

Table 10. GRAVITY SETTLING DESIGN DATA

Initial Solids Concentration. 1500 mg/l
Flow. . . . . 1 mgd
Overflow Concentration . . . 10 mg/l

Concentration of Underflow, mg/l	Solids Flux, lb./ft.^{2}/day	Area, ft.^{2}	Rate Overflow, mgd
3,000	2.87	4,359	0.498
4,000	2.45	5,106	0.373
5,000	2.25	5,560	0.299
6,000	2.06	6,073	0.249
7,000	2.00	6,255	0.213
8,000	1.95	6,415	0.186
9,000	1.89	6,619	0.166
10,000	1.84	6,800	0.149

Table 11. COMPARISON OF ACTIVATED CARBONS REMOVAL OF ORGANICS FROM STREAM 2

C_o = 50 mg/l TOC (Total Organic Carbon)
0.05 gms carbon/250 mls waste water

Carbon	Adsorptivity, mg TOC/g C
Witco 517	84
Calgon FS-300	76
Barneby Chaney - PC	72
Westvaco - WV-G	67
Westvaco WV-W	61
Hydrodarco HD-3000	55
Calgon FS-400	42

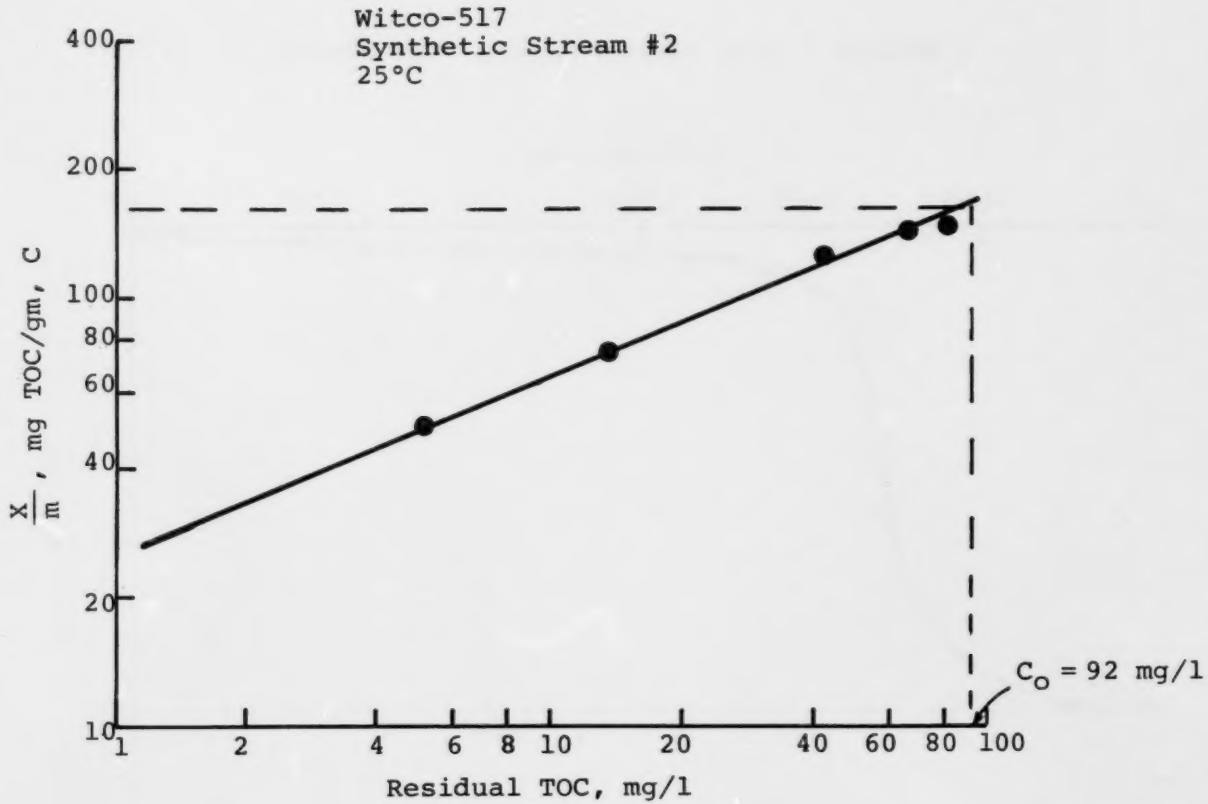


Figure 20. CARBON ADSORPTION ISOTHERM - STREAM 2

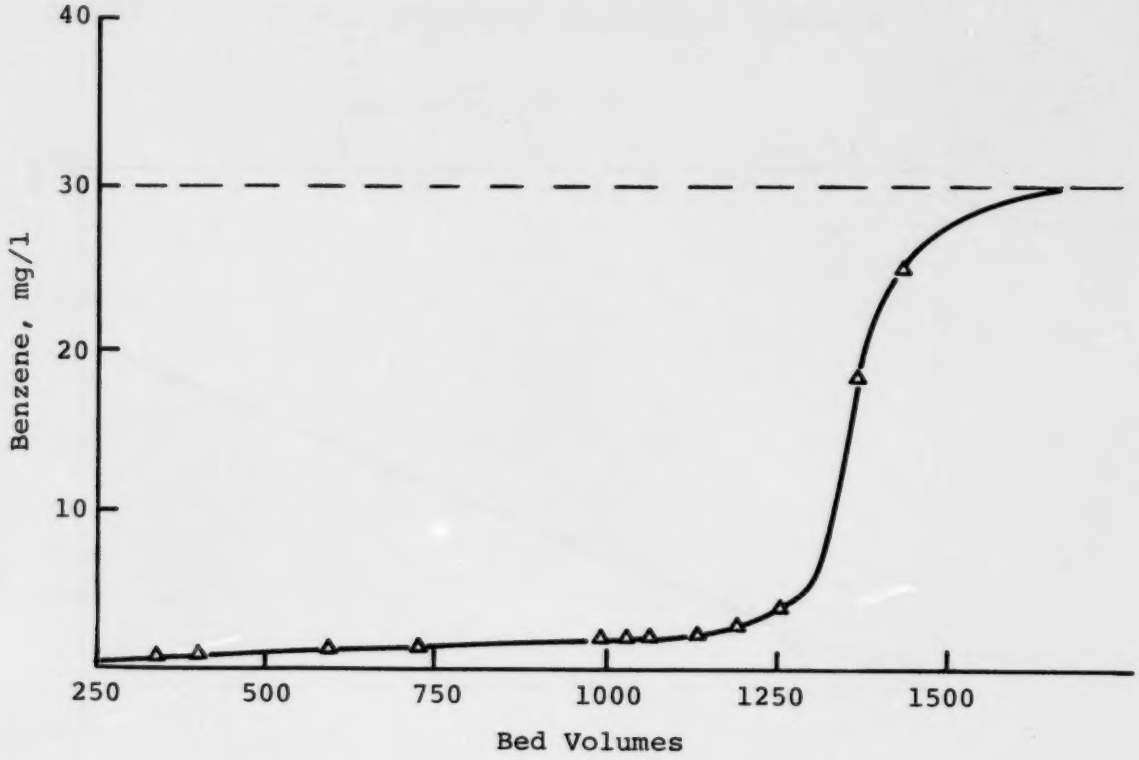


Figure 21. CARBON COLUMN TEST - STREAM 2

B. ELECTRODIALYSIS-REVERSE OSMOSIS STUDIES - STREAM 2

The electrodialysis unit used for these experiments was an Asahi Chemical Ind. Model SV-4 laboratory unit. This unit is larger than the SV-5 used to study Stream 1. It has 10 cell pairs with an active membrane area of 2 dm^2 as compared to 5 cell pairs of 0.75 dm^2 active membrane area for the SV-5 unit.

The reverse osmosis equipment was the same as used in the evaluation of Stream 1 treatment. The SV-4 unit was more closely matched to the reverse osmosis unit in capacity than the SV-5 unit used previously.

Because of the high concentration of NaCl in Stream 2, 4.5 percent NaCl, the units were first tested with a standard 4.5 percent NaCl solution to define the operating parameters. The E.D. unit operated at 0.58 volts/cell pair, and a current density of 2.5 amps/dm^2 producing a dilution stream of 4900 mg/l NaCl and a brine stream of 14.3 percent NaCl. The current efficiency was 87.4 percent and the limiting current density was 3.65 amps/dm^2. The RO unit was operated with a 4000 mg/l NaCl brine at 97.4 percent rejection and 50 percent product recovery. The NaCl concentration in the reject was 7400 mg/l and the product concentration was 240 mg/l.

Continuous ED-RO Operation on Pretreated Stream 2

The electrodialysis unit was operated to produce a dilution stream of 9000 mg/l NaCl, which was fed continuously to the RO unit. The reject from the RO unit was 1.5 percent NaCl and a product water of less than 500 mg/l NaCl was obtained. This run was continued except that the dilution concentration was lowered to approximately 6000 mg/l. The same feed was used. The experiment was allowed to run for 120 hours. The results are given in Table 12. Figure 21 is a plot of the critical operating parameters. Table 13 presents a detailed analysis of the various streams.

The operation of the units for 120 hours was uneventful. The current density was close to the 2.05 amp/dm^2 obtained during the standard run. The current efficiency continued to decrease throughout the run due to a steady decrease in brine production possibly from leakage. Inspection of the membrane showed no fouling or scaling. The calcium and magnesium ion present in the feed were transported to the brine along with the sulfate ion. Only traces of these ions showed up in the reverse osmosis product.

C. TOTAL RECYCLE SYSTEM DESIGN AND COST ESTIMATE

A flow diagram of the total recycle system of Stream 2 is given in Figure 23, which includes a material balance and flow rates of each stream. Centrifugation of the underflow of the gravity

Table 12. CONTINUOUS ELECTRODIALYSIS-REVERSE OSMOSIS RUN PRETREATED, STREAM-2 LOW DILUTION CONCENTRATION RESULTS

Electrodialysis Unit:	
Cell pairs	- 10
Feed NaCl	- 41,800 mg/l
Feed Rate	- 29 ml/min.
Dilution Recycle Rate	- 8.0 l/min.
Dilution Temperature	- 24.0°C
Brine Production Rate	- 7.3 ml/min.
Dilution NaCl	- 4,700 mg/l
Brine NaCl	- 146,000 mg/l
Current Density	- 1.95 amp/dm^2
Volts/cell pair	- 0.52
Reverse Osmosis Unit:	
Reverse Osmosis Pressure	- 195 psi
Feed Flow	- 42 ml/min.
Feed pH	- 6.0
Product Flow	- 23 ml/min.
Reject Flow	- 19 ml/min.
Reject NaCl	- 7,850 mg/l
Product NaCl	- 140 mg/l
Recovery	- 55%
NaCl Rejection	- 97.9%

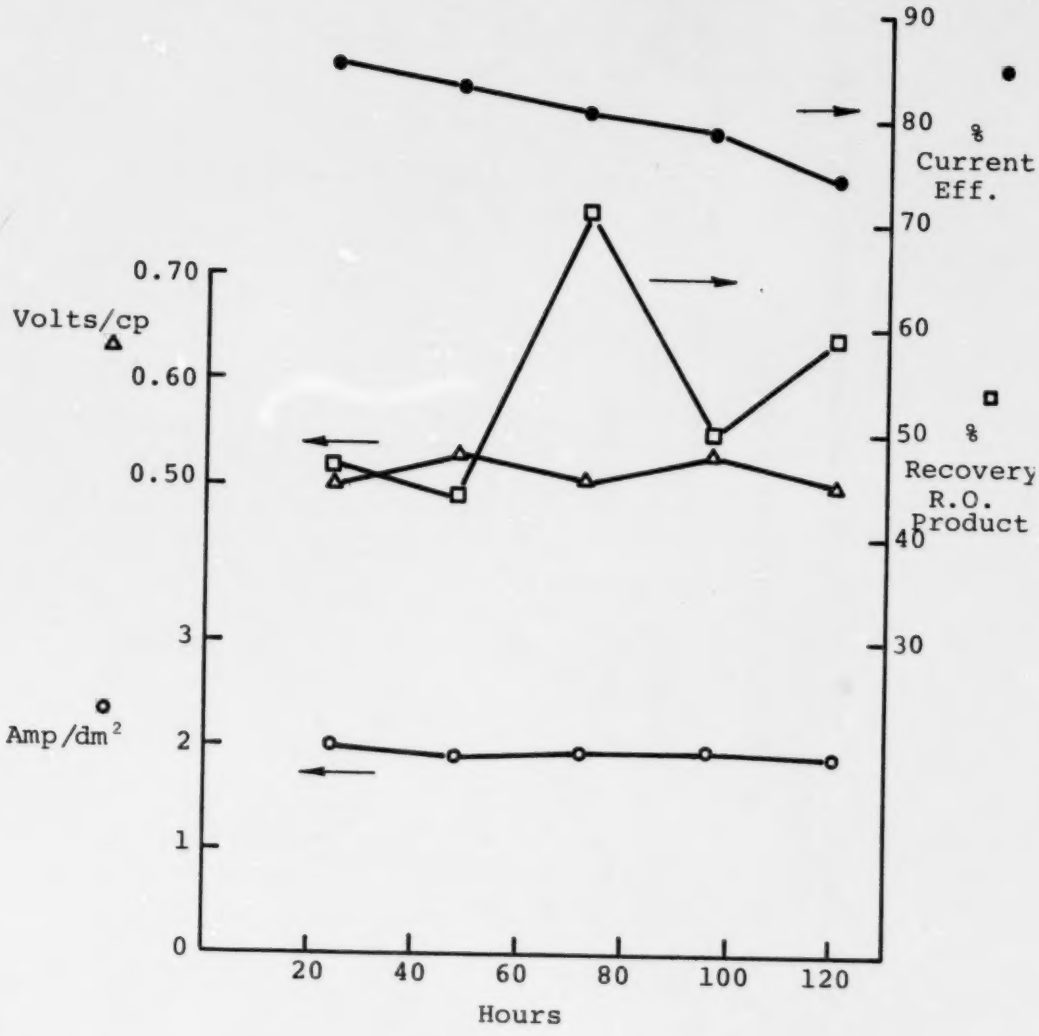
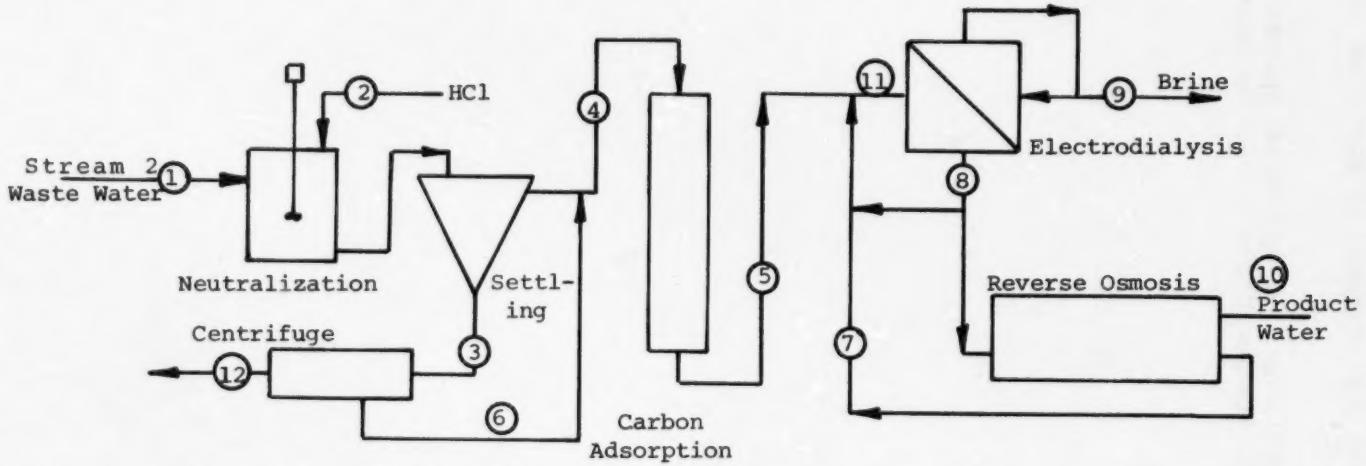


Figure 22. CONTINUOUS E.D.-R.O. PRETREATED STREAM 2

Table 13. CONTINUOUS ELECTRODIALYSIS-REVERSE OSMOSIS RUN WITH PRETREATED STREAM 2

Average Analysis of Streams

Parameter	Feed	Dilution	Electrodialysis Brine	Reverse Osmosis Product	Reverse Osmosis Reject
NaCl, mg/l	11,800	4,700	146,000	140	7,850
Mg^{++}, mg/l	0.2	--	<2	0.2	--
Ca^{++}, mg/l	8.5	--	96	0.5	--
Fe^{++}, mg/l	0.07	--	0.6	0.05	--
$SO_4^{=}$, mg/l	90	--	317	<1	--
TOC, mg/l	12	--	4	1	--
Silica, mg/l	2	--	--	--	--



	Units	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩	⑪	⑫
NaOH	lb/hr	1,720	--	--	--	--	--	--	--	--	--	--	--
HCl	lb/hr	--	1,324	--	--	--	--	--	--	--	--	--	--
Al^{+3}	lb/hr	240	--	240	0	--	--	--	--	--	--	--	240
TOC	lb/hr	30	--	9	29	6	8	--	--	6	--	--	1
NaCl	lb/hr	14,564	--	14,454	13,734	13,734	3,340	1,700	1,790	13,730	30	15,520	1,114
H_2O	lb/hr	332,494	2,256	100,425	309,638	309,638	75,313	164,922	380,210	94,270	215,348	474,480	25,112
Total	lb/hr	347,500	3,580	105,126	323,401	323,378	788,444	166,622	382,000	108,000	215,378	490,000	26,282
Sp Gr	1.02	1.19	1.02	--	1.02	1.02	1.02	1.01	1.01	1.10	1.0	1.02	--
Flow	mgd	1.0	.0103	.030	0.934	0.934	0.227	0.480	1.10	0.31	0.62	1.410	.076

Figure 23. TOTAL RECYCLE SYSTEM - STREAM 2

settler is included as a concentration step and was designed based on limited data obtained in the laboratory testing.

A summary of the estimated capital and operating costs of the total system is given in Table 14.

Details of the design and cost estimates of the unit operations required for the total recycle of Stream 2 are given in Appendix E.

Table 14. COST FOR TOTAL RECYCLE SYSTEM - STREAM 2

	1975 Dollars
Capital Cost:	
Neutralization and Solids Removal	$ 250,000
Carbon Adsorption	1,017,000
Electrodialysis-Reverse Osmosis	7,903,000
Total	$9,170,000
Operating Costs:	
Neutralization and Solids Removal	123,700
Carbon Adsorption	407,000
Electrodialysis-Reverse Osmosis	1,763,000
Total	$2,293,700 $/yr.

SECTION 7

ECONOMIC EVALUATION -- BRINE AND POTABLE WATER REUSE

In order to make a cost comparison of the ED-RO system, calculations have been made on four different feed water salt concentrations. The study was further expanded by setting permeate concentrations at 500 and 1500 mg/l NaCl to demonstrate the effect of product water quality on process economics. The cost does not include pretreatment, as this varies with different types of streams. Feed flow is 1 MGD.

Figure 24 shows the relationship of operating cost (including capital amortization) per 1000 gallons of Stream 1 waste water treated versus feed brine normality. The two product water concentration restrictions are shown, as well as a theoretical curve based on the higher current density achievable with an ideal NaCl feed.

Making a change in perspective from a waste treatment plant to one which produces process water, a similar cost analysis was made. Figure 25 is a plot of cost (in dollars) per 1000 gallons of permeate versus feed brine normality. There is a marked difference at higher normalities between the Stream 1 waste and the ideal NaCl brine.

To examine a salt production plant, another plot, Figure 26, was made of cost per 1000 pounds of NaCl (produced as a 13-14 percent brine) versus feed brine normality. The three Stream 1 plots are combined in Figure 27.

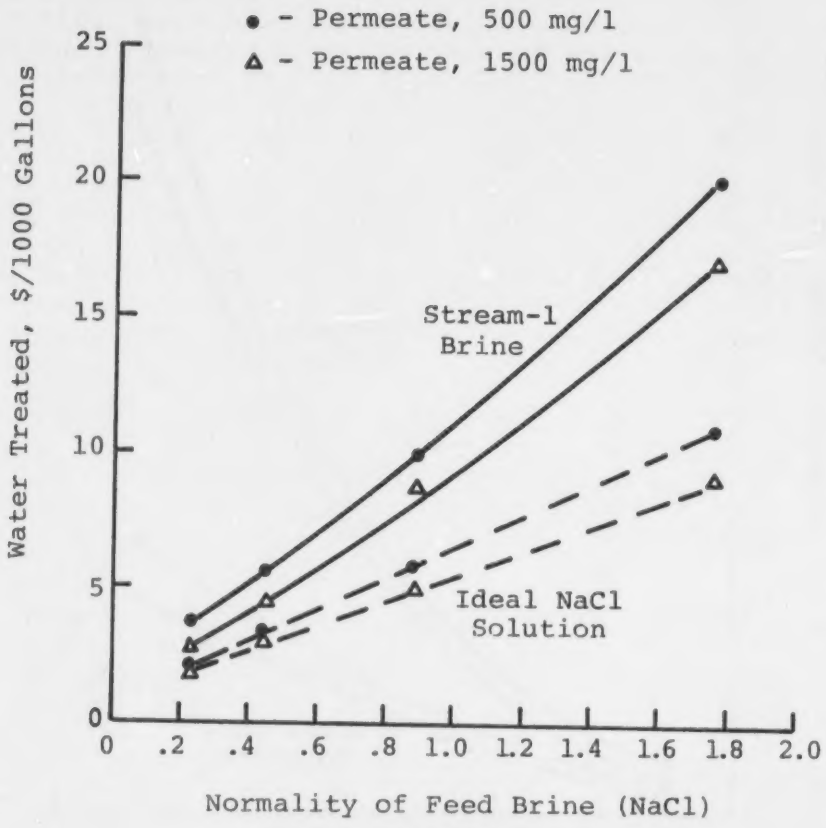


Figure 24. COST OF ED--RO OF BRINE SOLUTIONS - WATER TREATMENT

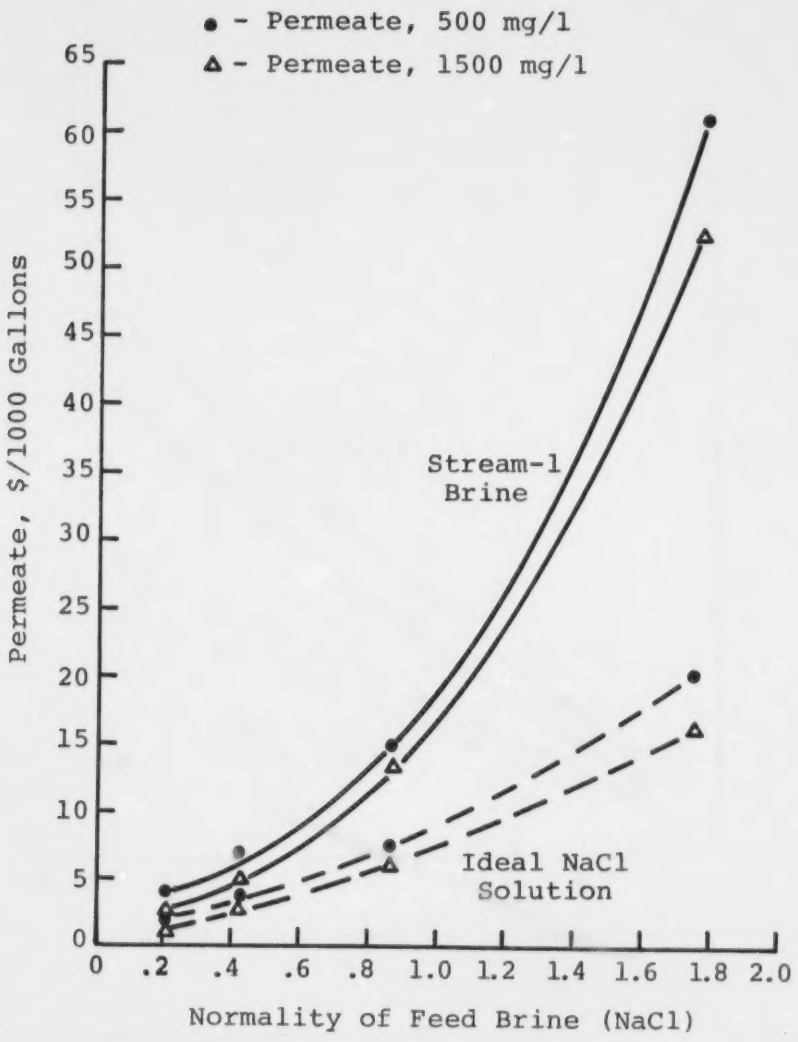


Figure 25. COST OF ED-RO OF BRINE SOLUTIONS - PRODUCTION OF PROCESS WATER

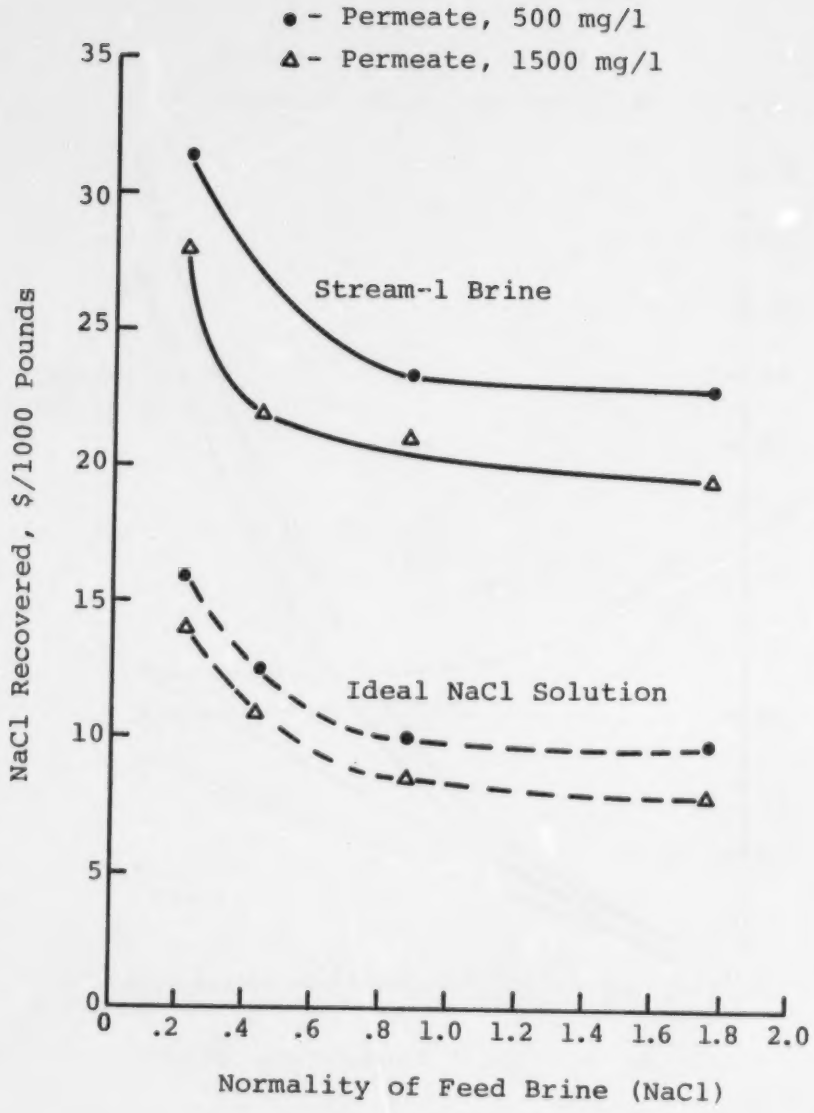


Figure 26. COST OF ED OF BRINE SOLUTIONS SALT PRODUCTION

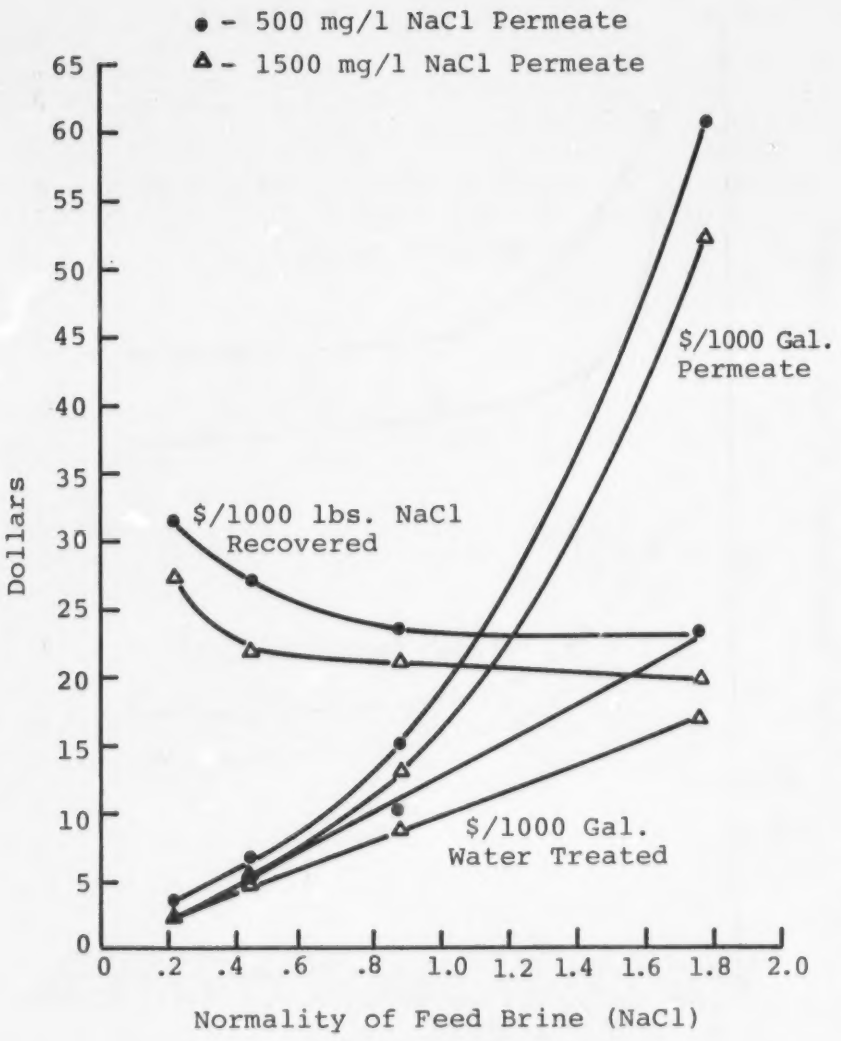


Figure 27. COST OF ED-RO TREATMENT OF STREAM-1

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Hochhauser, A. M., "Concentrating Chromium with Luquid Surfactant Membranes," Ph.D. dissertation, University Microfilms No. 74-20,365, Ann Arbor, Michigan, 1974.

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McLaren, J. R. and G. J. Farquhar, "Factors Affecting Ammonia Removal by Clinoptilolite," Journal of the Environmental Engineering Division, 429, August 1973.

Mercer, B. W. L. L. Ames, W. J. Touhill, W. J. VanSlyke, and R. B. Dean, "Ammonia Removal from Secondary Effluents by Selective Ion Exchange," Journal WPCF, 42(2), part 2, 1970.

Schiffer, D. K., A. Hochhauser, D. F. Evans, and E. L. Cussler, "Concentrating Solutes with Membranes Containing Carriers," Nature, Vol. 250, August 9, 1974.

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Wang, L. K-P, D. W. Goupil, and M. S. Wang, Purdue University Engineering Extension Series, Vol. 141, Part 1, 569-578, 1972.

Appendix A
CONVERSION TABLE

Multiply	By	To Obtain
Barrels (bbls.)	158.98	Liters (l)
Feet (ft.)	.3048	Meters (m)
Feet per hour (ft./hr.)	0.508	Centimeters per minute (cm/min.)
Gallons (gal.)	3.785	Liters (l)
Gallons per day (gpd)	3.785	Liters per day (l/day)
Gallons per minute (gpm)	3.785	Liters per minute (l/min.)
Gallons per minute per square foot ($gpm/ft.^2$)	40.74	Liters per minute per square meter ($l/min./m^2$)
Inches (in.)	2.54	Centimeters (cm)
Pounds (lb.)	0.4536	Kilograms (kg)
Pounds per cubic foot ($lb./ft.^3$)	16.02	Kilograms per cubic meter (kg/m^3)
Pounds per day (lb./day)	0.4536	Kilograms per day (kg/day)
Pounds per hour (lb./hr.)	0.4536	Kilograms per hour (kg/hr.)
Pounds per square foot per day ($lb./ft.^2$)	4.882	Kilograms per square meter per day ($kg/m^2/day$)
Pounds force per square inch (psia)	0.07031	Kilograms force per square centimeter (kg/cm^2)
Standard cubic feet (scf)	26.79	Liters at STP (l)

Appendix B
ANALYTICAL METHODS

Standard analytical procedures were used for the routine analysis of pH, total alkalinity, acidity, total dissolved solids (TDS), suspended solids, chloride ion, organic nitrogen (Kjeldahl nitrogen), ammonia nitrogen, oil and grease and APHA color. Sulfate ion in high concentration was analyzed using the benzidine-dihydrochloride method. In low concentrations, sulfate ion was determined by using an ion chromatograph. Trace metal ions were determined using emission spectroscopy.

In the case of Stream 1, a method was required for the analysis of sodium hydroxide exclusive of the amines present. A non-aqueous titration method was developed for this analysis.

The analysis of the organic constituents of the petrochemical waste waters was more difficult to perform and to interpret. The characterization of the organic content of the waste waters required the use of gas chromatographic methods to identify and quantify the organic compounds present. A gas chromatographic method was developed for the analysis of the organics in Stream 1 and Stream 2. Conditions of GC analysis of Stream 2 are given in Table B-1.

Other methods were used to monitor the organic content of the waste waters. Total organic carbon (TOC), inorganic carbon (IC), and total carbon (TC) were determined using a Beckman Model 915 carbon analyzer. The method entails the injection of a micro sample into a catalytic combustion tube at 950°C. The carbon-aqueous material is oxidized to carbon dioxide in a carrier stream of air. The amount of CO_2 produced is directly proportional to the amount of carbonaceous material in the injected sample and is measured by a sensitized infrared analyzer. This determines the total carbon. A second injection of the sample is made into a low temperature oven tube containing phosphoric acid and the inorganic carbon is released and purged by an air stream to the infrared detector. This determines the inorganic carbon. The difference between the two values is the total organic carbon.

Total oxygen demand (TOD) was also used to determine the organic content of the waste waters. An Ionics Model 225 Total Oxygen Demand analyzer was used. The determination is made by injecting a micro sample of the waste water in a combustion tube containing a platinum catalyst at 950°C. The catalyst tube is continually

purged with a flow of nitrogen contaminated with a low concentration of oxygen. The oxidation of the carbon in the injected sample causes a decrease in the oxygen level in the nitrogen stream. This will register as a change in electrical output from a silver-lead fuel through which the nitrogen stream flows. This response is proportional to amount of oxidizable organic carbon present in the sample.

Table B-1. GAS CHROMATOGRAPHIC ANALYSIS CONDITIONS - STREAM 2

Gas Chromatograph	-	Hewlitt-Packard 5711A
Detector	-	Dual FID
Injector Temperature	-	110°C
Detector Temperature	-	300°C
Columns	-	12 ft. x 1/8, SS
Column Packing	-	10% Carbowax 20M on Chromosorb W-HP 80-100 mesh
Oven Temperature	-	Isothermal 110°C
Carrier Gas	-	Helium
Carrier Gas Flow Rate	-	30 cc/min. at 60 psi
Air Flow Rate	-	240 cc/min. at 24 psi
Hydrogen Gas Flow Rate	-	30 cc/min. at 15 psi
Sample Injection	-	3 microliters of 1:1 CS_2 extract of the sample
Calculation	-	Integration and calculation performed by HP 3380A Integrator-Recorder
Retention Times	-	Benzene - 1.75 min. Ethylbenzene - 5.05 min.

Appendix C
AMMONIA REMOVAL

A. Literature Review

Several processes are presently used for ammonia removal from waste waters. The concentration of ammonia is an important factor in determining which process to use.

For ammonia concentrations of the order of several percent, stream stripping in a column desorber with countercurrent flow is generally used. A wet ammonia overhead is obtained which can be recycled directly or condensed to produce an aqueous solution. Effluent waste water can be expected to contain about 1000 ppm ammonia. Secondary stripping is used to reduce the effluent level to near 50 ppm ammonia. The secondary stripper overhead can be used as a steam source for the primary desorber. This degree of ammonia removal may be sufficient in some cases, but frequently it is not.

To remove ammonia from waste waters containing concentrations in the 100 ppm or less range, four processes have been used. These are air stripping, nitrification-denitrification, selective ion exchange, and breakpoint chlorination.

Air stripping is generally accomplished in a countercurrent or crosscurrent flow tower very similar to a water cooling tower. Large fans draw air through waste water that trickles through slats of wood or plastic, desorbing the ammonia. The pH of the waste water is adjusted to a value near eleven, usually with lime. This converts all ammonium ions to dissolved ammonia. The air requirement is of the order of 300 cu.ft. per gallon of liquid. The air stripping process is simple and reliable, and removals range from 60 to 95 percent. The removal efficiency at low temperatures is poor because ammonia solubility is inversely related to the temperature. If lime is used to raise the pH, scaling may be a problem. The discharge of ammonia into the atmosphere can be prevented, if necessary, by scrubbing the ammonia-rich gas.

Nitrification-denitrification is accomplished by biological oxidation of the ammonia to nitrite or nitrate, followed by biological reduction to nitrogen gas. This process can be carried out in various biological reactor systems, and as in all microbiological reactors, the major operational difficulty encountered is insolubility. The nitrification step is aerobic, while the

denitrification step is anaerobic. A substrate, such as methanol, must be added to the waste for denitrification to occur. Ammonia removal efficiencies range from 80 to 98 percent.

In the breakpoint chlorination process, the ammonia is oxidized to various chloramines, and then to nitrogen gas. About 10 parts of chlorine are required for every part of ammonia-nitrogen that is reacted. Dechlorination may follow chlorination to remove residual chlorine, or carbon adsorption to remove unoxidize chloramines. For high concentrations of ammonia, breakpoint chlorination is not economical because of chlorine costs. However, removal efficiencies of 90 to 100 percent have been reported, and this process is often used following one of the previously mentioned processes to reduce the residual ammonia level to near zero.

B. Ammonia Removal Tests

1. Liquid membrane process

A process by which both the ammonia and the amines could be removed and recovered simultaneously would be of great value in pretreating this waste water. One process that offers this possibility is the liquid surfactant membrane process described by Li and Shrier (1972).

A schematic diagram of the conceptual Liquid Membrane Water Treatment Process is shown in Figure C-1.

Liquid surfactant membranes are formed by first making an emulsion of two immiscible phases such as a water and an oil. A surfactant is added to stabilize the emulsion. The emulsion is then dispersed into a third phase. The liquid membrane phase refers to the phase between the encapsulated phase in the emulsion and the third phase. The encapsulated phase and the third phase are usually miscible but are immiscible with the membrane phase. The liquid membranes can be modified for specific applications and the large surface area of the membrane allows rapid permeation and equilibration during mixing. Facilitated transport can be used to enhance this mass transfer. This involves encapsulation of a reagent within the membrane that reacts with the permeating specie and forms a specie that will not permeate. After sufficient contact time between the emulsion and the third phase, mixing is stopped and the phases are allowed to separate. The emulsion can then be decanted off the top and de-emulsified to release the permeated specie.

Li, N. N. and A. L. Shrier. "Liquid Membrane Water Treating", Recent Developments in Separation Science, Vol. 1, CRC Press,1972.

Cahn, R. P. and N. N. Li. "Separation of Phenol from Waste Water by the Liquid Membrane Technique," Separation Science, 9(6), 505-519, 1974.

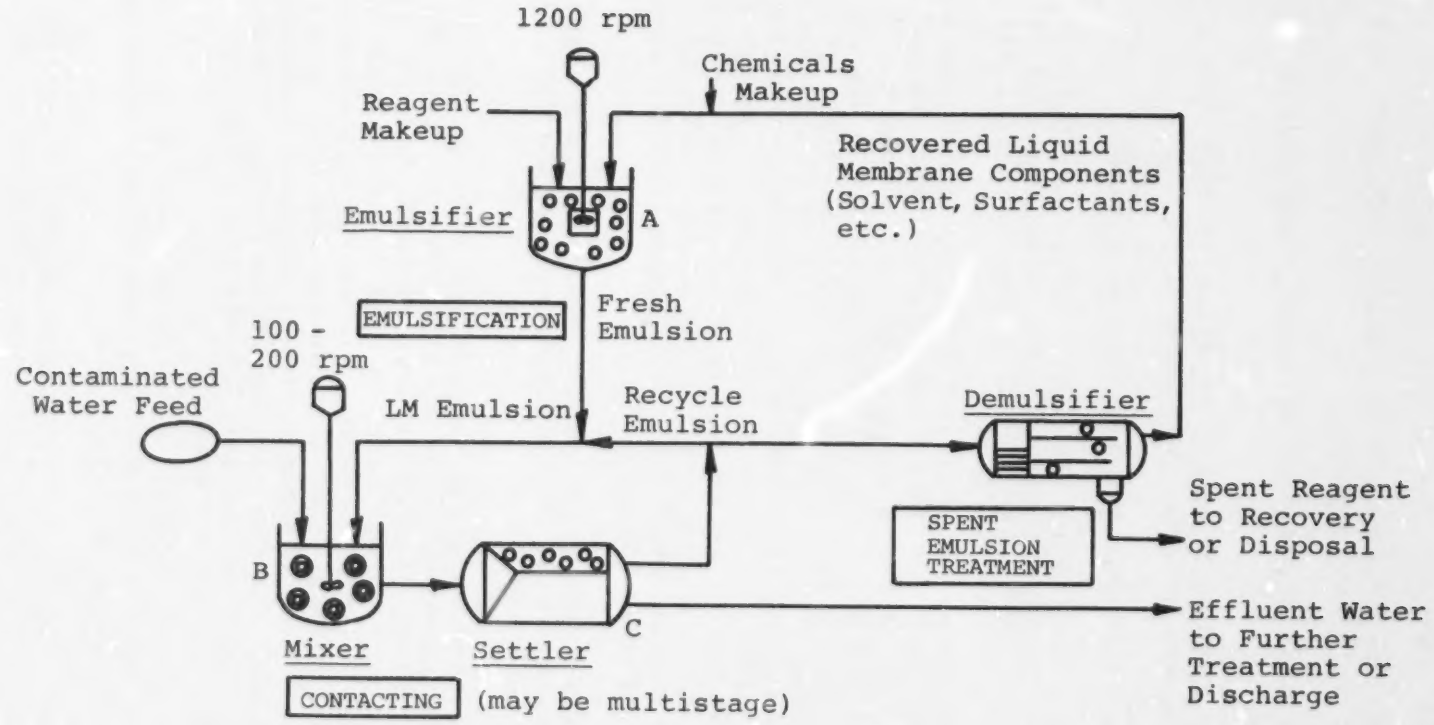


Figure C-1. SCHEMATIC DIAGRAM OF CONCEPTUAL LMWT PROCESS

Liquid membranes have been demonstrated (Li and Shrier, 1972; Cahn and Li, 1974) to:

1. Remove weak acids such as phenol, H_2S, HCN, and acetic acid from water.

2. Remove weak bases such as ammonia and amines from water.

3. Purify hydrocarbons and separate toluene from heptane and benzene from hexane.

4. Remove suspended solids from waste water.

5. Remove selectively chromium, cupric, mercuric, silver, sulfide, nitrate, and phosphate ions from water (Schiffer, et al, 1974; Hochhauser, 1974).

A synthetic waste water containing 160 mg/l ammonia and 1000 mg/l ethylene diamine in pH 12 caustic was treated with liquid surfactant membranes. The membrane was produced by adding at 10 ml/min, approximately 80 mls of 0.1 N hydrochloric acid to approximately 160 mls of S-100-N oil containing 2 percent by weight SPAN® 80. The mixing was done at 1300 rpm using a Fisher Stedi-Speed Model 12 stirrer. The mixing continued for 10 minutes after the last of the acid was added. A thick milky white emulsion was formed. The resulting 250 mls of emulsion was mixed with 250 mls of synthetic waste water at 200 rpm. Samples were taken of the aqueous phase at timed intervals. These samples were analyzed for ammonia and ethylene diamine.

Table C-1 summarizes the experimental conditions and results. Figure C-2 presents a plot of the Ct/Co versus the time of contact with the liquid membrane.

The results indicated that the ammonia was removed within 5 minutes and the maximum ethylene diamine removal occurred in 15 minutes. The ethylene diamine removal stopped short of complete removal because there was not enough acid to react with the remaining ethylene diamine. Membrane breakage and subsequent neutralization of the acid may account for the fact that only 94 percent of the acid was reacted when the permeation stopped. The concentration factor for ammonia was approximately 3 because the ammonia that was contained in the 250 mls was transferred in the 80 mls of acid within the membrane.

Schiffer, D. K., A. Hochhauser, E. F. Evans, and E. L. Cussler, "Concentrating Solutes with Membranes Containing Carriers," Nature, Vol. 250, August 9, 1974.

Hochhauser, A. M. "Concentrating Chromium with Liquid Surfactant Membranes," Ph.D. dissertation, University Microfilms No. 74-20, 365, Ann Arbor, Michigan, 1974.

Table C-1. LIQUID MEMBRANE TREATMENT OF SYNTHETIC STREAM 1 WASTE WATER

Volume of liquid membrane taken	250 mls
Volume of waste water taken	250 mls
Total time of experiment	60 minutes
Initial ammonia concentration	160 mg/l
Final ammonia concentration	0 mg/l
Ammonia removed	100%
Initial ethylene diamine concentration	1000 mg/l
Final ethylene diamine concentration	380 mg/l
Ethylene diamine removed	62%
Ammonia removed	2.35 meq
Ethylene diamine removed	5.17 meq
Total removed	7.52
Total meq of HCl available	8.0
HCl usage	94%
Concentration factor-ammonia	3

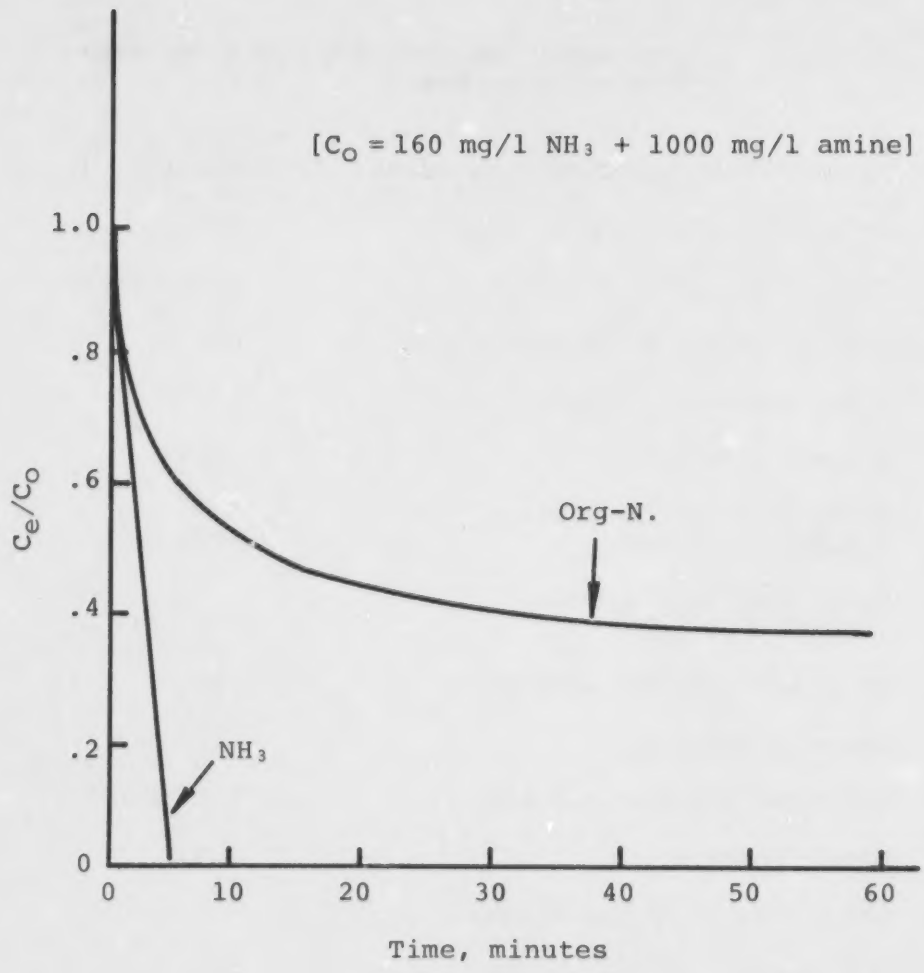


Figure C-2.SYNTHETIC STREAM 1 - WASTE WATER
LIQUID MEMBRANE TREATMENT

Although the initial experiment showed some promise for this technique, attempts to increase the concentration factor by encapsulating a higher concentration of hydrochloric acid in the membrane were unsuccessful. The liquid membrane formed was too unstable. Experiments with waste water which contained a higher sodium chloride level than the synthetic also failed because of membrane instability. No experiments were run to determine the ease with which the exhaust liquid membrane could be de-emulsified to recover the ammonia and amine hydrochlorides.

Further extensive work will be required to develop a liquid surfactant membrane which remains stable in the presence of higher HCl concentrations and higher brine waste waters.

2. Ion exchange

One other method of ammonia removal from waste water was tried. This was the use of clinoptilolite as an ion exchanger to remove ammonium ions from the water. This process has been described variously in the literature in conjunction with removal of ammonia from municipal waters (Mercer, et al, 1970; McLaren and Farquhar, 1973; Battelle-Northwest, 1971). A supply of clinoptilolite was obtained and prepared (McLaren and Fraquhar, 1973). A small column was filled with 20 grams of resin. A flow rate of 1 gpm/sq.ft. was set. The feed solution neutralized Stream 1 waste water. Figure C-3 shows the results of this experiment. The exchange capacity was found to be 0.28 meq. of ammonia-nitrogen/gm. of resin, much less than the capacity (1.6-1.8 meq./g.) given by the supplier (McLaren and Farquhar, 1973). A value of 0.95 meq./g. was obtained for a water containing 70 mg/l. ammonia-nitrogen.

Apparently at the higher ion concentration of the waste water, the cations compete with the ammonia for exchange sites and the capacity of the resin for the ammonia ion is much too low to be used to remove ammonia from Stream 1 waste water.

Mercer, B. W. et al. "Ammonia Removal from Secondary Effluents by Selective Ion Exchange," Journal WPCF, 42(2) Part 2, 1970.

McLaren, J. R. and G. J. Farquhar. "Factors Affecting Ammonia Removal by Clinoptilolite," Journal of Environmental Engineering. 429, August, 1973.

Battelle-Northwest, "Wastewater Ammonia Removal by Ion Exchange," EPA-Water Pollution Control Series No. 17010 ECZ 02/71, 1971.

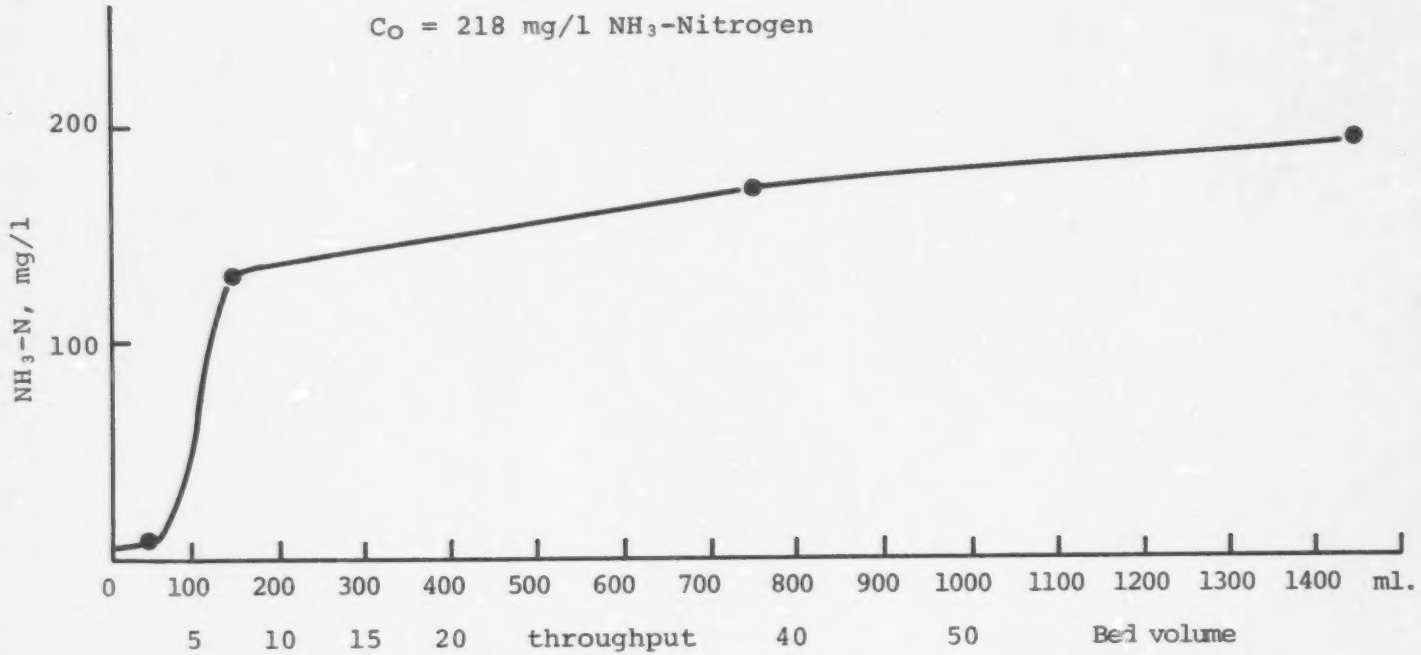


Figure C-3. EXCHANGE OF NH_4^+ ON CLINOPTILOLITE FROM STREAM 1 WASTE WATER

Appendix D
TOTAL RECYCLE SYSTEM DESIGN AND COST ESTIMATES FOR STREAM 1

The process design of the unit operations required for the total recycle of Stream 1 are based on a flow rate of 1 MGD wastewater. A cost estimate of the total system is made based on 1975 costs.

A. Pretreatment Design

1. Carbon adsorption

The bed depth-service time, for 95 percent TOC removal is plotted in Figure D-1. One column test was run at the lower rate of 1 gpm/ft^2 and the rest were made at 2 gpm/ft^2. The agreement between the values obtained from the actual 2 gpm/ft^2 run and those calculated from the 1 gpm/ft^2 converted to 2 gpm/ft^2 was excellent. From the results of the electrodialysis-reverse osmosis tests, it was evident that the TOC removal must be maximized. This is why 95 percent removal was selected. The design bed versus service time relationship for 95 percent removal was:

$$t = 0.38(x) - 1.25$$

where:

t = service time, hours
x = bed depth, feet

The carbon treatment unit is designed for a linear flow rate of 4 gpm/ft^2, to handle 1 MGD of wastewater, of 1650 mg/l feed TOC, producing a TOC concentration of 80 mg/l. The activated carbon is Westvaco WV-G, 12 x 40 mesh of 25 lbs/cu.ft. density.

The cross-sectional area requirement is:

$$500{,}000 \text{ gpd} / (4 \text{ gpm/ft}^2)(1440 \text{ min/day}) = 87 \text{ ft}^2$$

(The area for a 1,000,000 gpd unit was too great, so the process unit will be divided into two parallel trains. Each will treat 500,000 gpd.)

The carbon bed volume will be:

$87 \text{ ft}^2 \times 20 \text{ ft.}$ (bed depth) $= 1740 \text{ ft}^3$

The adsorber volume will be (50% higher for backwash)

$1740 \text{ ft}^3 \times 1.5 = 2610 \text{ ft}^3$

The adsorber dimensions:

30 ft x 10.5 ft I.D.

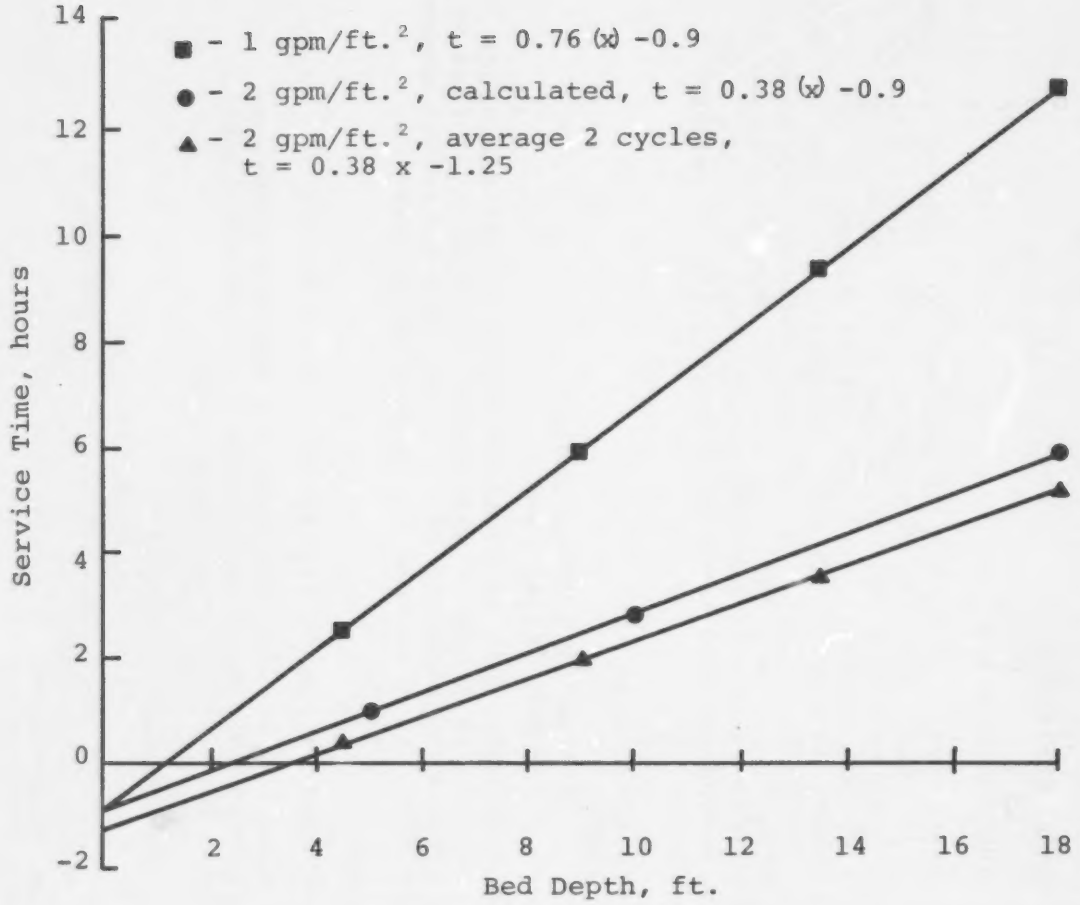


Figure D-1. ACTIVATED CARBON TREATMENT OF STREAM 1

The bed dimensions will be:
20 ft x 10.5 ft I.D.
The weight of the carbon per bed will be:
1740 ft^3 x 25 lbs/ft^3 = 43,500 lbs
The bed service time will be:
t = 0.19(20) - 1.25 = 2.5 hours

Three columns in series will operate for approximately 8 hours or one shift. Each one will need to be regenerated once per shift. A fourth column will be needed for the regeneration. To handle the 1 MGD of Stream 1, two trains of four columns will be needed. Three columns will be in operation at one time while one column in each train is being regenerated.

The acid requirement for the regeneration of the carbon was determined to be 1.8 bed volumes of acid per regeneration. However, 0.3 bed volumes are recycled back to the acid tank so 1.5 bed volumes is actually used. Approximately 10 regenerations will be required per day per train or 20 all together. Therefore, 30 bed volumes of 30 x 13,000 gal. will be required per day. This is 390,000 gallons of 2 N acid or 65,000 GPD of concentrated acid (12 N).

Figure D-2 shows a flow diagram and material balance for one train of the process.

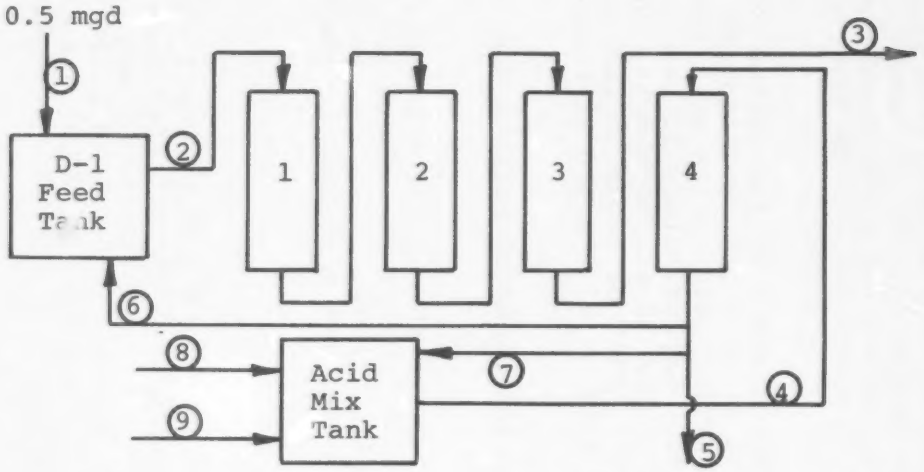
The capital cost for the carbon treatment includes adsorbers, pumps, carbon, tanks and associated equipment. These are shown in Table D-1. The operating cost includes utilities, amortization, labor, carbon replacement, and acid costs. These are shown in Table D-2.

2. Neutralization

The acid requirement for the neutralization of Stream 1 was determined to be 22 gal. of concentrated HCl per 1000 gals. of Stream 1. After carbon treatment, the stream volume was 1,180,000 gal. After neutralization, the stream rate will be 1,206,000. It will require 26,000 gal. of concentrated acid per day, or 9.5 Mgal/yr. The capital and operating costs for neutralization are given in Table D-3.

3. Silica removal

The design and costs are presented for silica removal. A 1.2 MGD stream after neutralization must be treated with an alumina column. Table D-4 is the design bases. Figure D-3 gives the process design and material balance. The process consists of two trains of two columns each. Each column is 16 ft. long x 11.5 ft. diameter. The bed volume is 1675 ft^3 and each contains 92,000 lbs. of F-1 alumina. Before regeneration, 190 bed volumes are treated with 1.5 bed volumes of caustic. Table D-5 gives the cost estimate for this process.



lbs/hr	①	②	③	④	⑤	⑥	⑦	⑧	⑨
NaCl	150	1,550	1,550	--	--	1,400	--	--	--
HCl	--	--	--	4,900	--	--	700	4,200	--
NaOH	1,500	1,500	1,500	--	--	500	--	--	--
TOC	300	330	15	1	280	30	5	--	--
H_2O	171,800	201,470	201,470	81,300	35,450	29,670	12,850	11,400	57,300
Organics	--	--	--	--	410	--	7	--	--
Total	173,750	205,350	205,035	86,200	36,140	31,600	13,550	15,600	57,300
Sp. Gr	1.01	1.01	1.01	1.03	1.03	1.03	1.03	1.19	1.0
Flow, gpd	500,000	590,000	590,000	234,000	104,000	91,000	39,000	32,700	465,000

Figure D-2. TOTAL RECYCLE SYSTEM STREAM 1 - CARBON TREATMENT PROCESS DESIGN AND MATERIAL BALANCE

B. Electrodialysis-Reverse Osmosis Design

The basis for the design to handle the pretreated Stream 1 waste is given in Table D-6. The material balance is given with the flow diagram presented in Figure D-4.

For the reverse osmosis unit, the capital cost is calculated as 0.65 dollars per gallon per day permeate and the operating cost as 0.60 dollars per 1000 gallons of permeate. For the electrodialysis unit, 2 presses 1800 cell pairs each are required. The cost per press of $500,000 times a factor of 2.5 gives the total plant cost.

A summary of the capital and operating costs of the reverse osmosis-electrodialysis hybrid is given in Table D-7.

Table D-1. 1-MGD STREAM 1 - ACTIVATED CARBON TREATMENT
ESTIMATE OF DIRECT CAPITAL COST

Item	Installed Cost
Adsorption Columns (8) at $200,000 each 30' x 10.5' dia. - Monel-Vertical Vessel	$1,600,000
Pumps (8)	15,000
Pumps - Acid Service (2), Monel	20,000
Carbon, Initial Charge - Westvaco WV-G, 12 x 40 Mesh, 348,000 lbs. at $.50	174,000
Feed Equilization and Storage Tank 1/2 Day Volume (10,100 bbl.)	78,000
Acid Storage Tank (2,100 bbl.) 8-Hour Capacity Rubber Lined Carbon Steel	54,000
General Services (10%)	190,000
Direct Capital	$2,131,000
Allocated Capital - Electric Power	50,000
Factory Expense (7% of Direct Capital)	149,000
FIXED CAPITAL	$2,330,000

Table D-2. 1-MGD STREAM 1 - ACTIVATED CARBON TREATMENT - ESTIMATE OF OPERATING COST

Item	Quantity	Cost per Unit	Cost per Year
Raw Materials			
HCl, 38%	9×10^7 lbs.	$0.02	$1,800,000
Carbon Replacement	34,000 lbs.	0.50	17,000
Operating Labor	4 Man-yrs.		100,000
Maintenance	6% of Process Equipment Capital		128,000
Power			20,000
River Water	60 M Gal.	0.025	2,000
Factory Expense	2.6% of Direct Capital		55,000
Taxes and Insurance	1.1% of Direct Capital		23,000
Depreciation	10% of Direct Capital		213,000
			$2,358,000

TOC Removed per year = 2.45×10^6 lbs.
Organics Recycled per year = 6.0×10^6 lbs.
Cost per lb. Organics Recycled = $.39/lb.
Value of Organics at 50¢ per lb.= $3,000,000 $/yr.

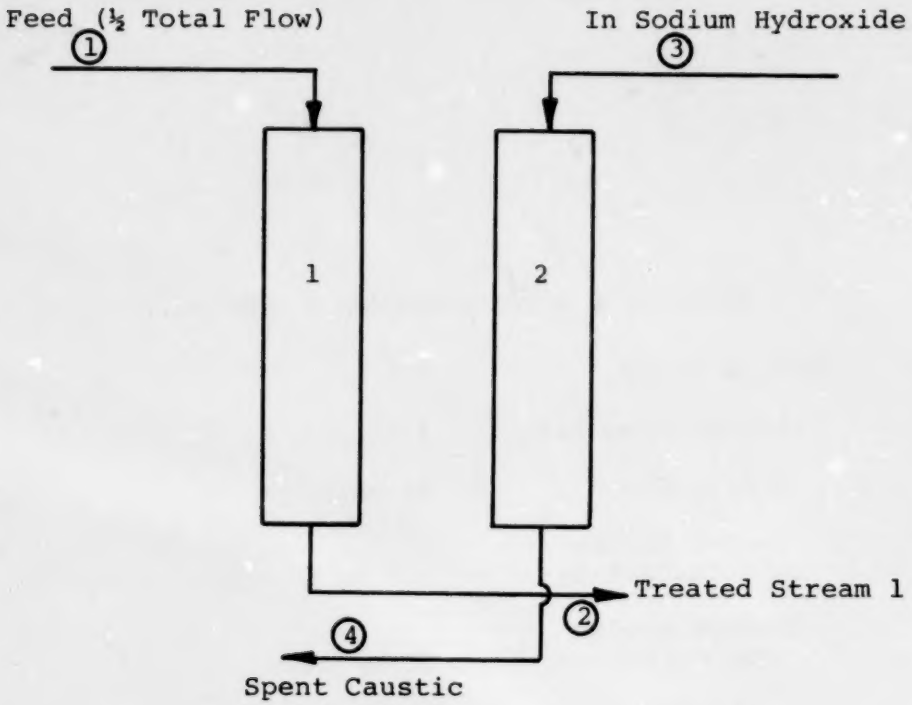
Table D-3. 1-MGD STREAM 1 - NEUTRALIZATION
ESTIMATE OF CAPITAL AND OPERATING COSTS

Item	Cost
Capital Cost:	
Mixing Tank - Rubber Lined 8-Hour Capacity, 400,000 gal.	$ 54,000
Pump - Acid Service, Monel	10,000
Pump	2,000
General Service (10%)	6,000
Direct Capital	$ 72,000
Allocated Capital, power	10,000
Factory Expense (7%)	5,000
FIXED CAPITAL	$ 87,000
Operating Cost:	Cost $/yr.
Raw Materials, HCl, 38% 9.4×10^7 lbs. at $0.02	$1,880,000
Maintenance (6%)	4,000
Power	5,000
Factory Expense (2.6%)	2,000
Taxes and Insurance (1.1%)	1,000
Depreciation (10%/yr.)	7,000
	$1,900,000 $/yr.

Table D-4. SILICA REMOVAL - STREAM 1

Design Basis:

Linear Flow Rate	-	4 gpm/ft.^{2}
Design Flow	-	50 mg/l
Design Silica Concentration	-	<10 mg/l
Design Product Concentration	-	30 minutes
Capacity	-	20 mg Silica/g Alumina
Bed Depth	-	16 ft.
Alumina	-	Alcon F-1
Density	-	55 lbs./cu. ft.



	Units	1	2	3	4
NaOH	lbs/hr	--	--	70	70
Silica	"	10.5	2.1	--	8.4
H_2O	"	208,490	208,490	1639	1621.6
Total	"	208,500	208,492	1700	1700
Flow	gpd	600,000	600,000	5000	5000

Figure D-3. TOTAL RECYCLE SYSTEM - STREAM 1
SILICA REMOVAL, DESIGN BASIS AND
MATERIAL BALANCE

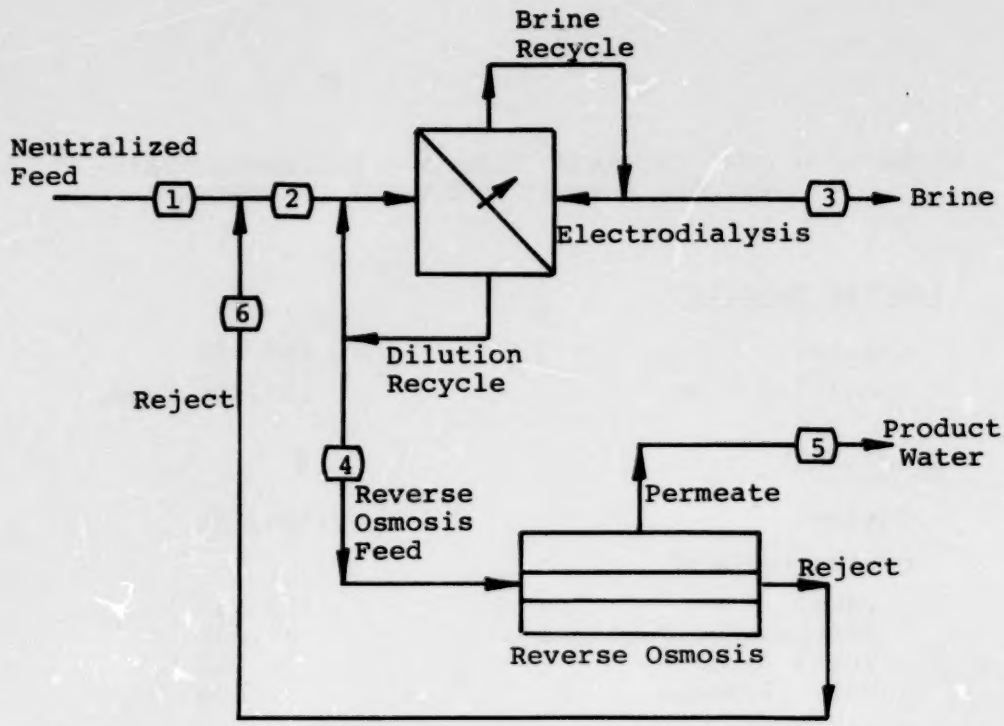
Table D-5. ACTIVATED ALUMINA TREATMENT OF STREAM 1 - ESTIMATE OF CAPITAL AND OPERATING COSTS

Item	Cost
Capital Cost:	
Four Adsorber Columns at $36,000 each (16' x 115' dia. - Carbon Steel)	$144,000
Caustic Mix Tank 1-Day Capacity - Carbon Steel	9,000
Two Pumps	4,000
Alumina, 370,000 lbs. at $0.15/lb.	56,000
General Services (10%)	22,000
Direct Capital	$235,000
Allocated Capital	10,000
Factory Expense (7%)	16,000
	$261,000
Operating Cost:	$/yr.
Raw Materials	
100% Caustic, 600,000 lbs.	$ 30,000
Water, 1,825,000 gallons	400
Maintenance (6% of Capital)	16,000
Power	5,000
Factory Expense (2.6%)	7,000
Taxes and Insurance (1.1%)	3,000
Depreciation (10%/yr.)	26,000
	$ 87,400

Table D-6. 1-MGD STREAM 1 - ELECTRODIALYSIS-REVERSE OSMOSIS DESIGN

Basis:

Design NaCl Feed Concentration	-	14,000 mg/l (0.24 N)
Design Brine Product	-	>140,000 mg/l Maximum 2.40 N
Design R.O. Product	-	<500 mg/l (0.009 N)
Feed Rate	-	1.2 mgd
Volts/cell pair	-	0.74
Current Density	-	1.6 amp/dm^2
R.O. Product Recovery	-	48%
NaCl Rejection	-	95%
Number of SS-O Press	-	2
Cell Pairs	-	3131
Operation	-	330 day/yr.



lb/hr	①	②	③	④	⑤	⑥
NaCl	5,850	8,720	5,700	3,020	150	2,870
H_2O	418,000	712,000	34,000	678,000	384,000	294,000
Total	423,850	720,720	39,700	681,020	384,150	296,870

Figure D-4. ELECTRODIALYSIS-REVERSE OSMOSIS OF PRETREATED STREAM-1, FLOW DIAGRAM AND MATERIAL BALANCE

Table D-7. COST ESTIMATE SUMMARY - ELECTRODIALYSIS-REVERSE OSMOSIS TREATMENT OF STREAM 1

Reverse Osmosis:		
Capital	$ 615,550	
Operating Cost	187,500	$/yr.
Electrodialysis:		
Capital	$2,500,000	
Operating Cost		
Power	133,530	
Membrane Replacement	87,000	
Total Labor	38,250	
Miscellaneous	50,000	
Depreciation	250,000	
Total	$ 458,780	$/yr.
ED-RO:		
Total Capital	$3,115,550	
Total Operating Cost	$ 646,280	$/yr.

Appendix E
TOTAL RECYCLE SYSTEM DESIGN AND COST ESTIMATES FOR STREAM 2

A total recycle system is designed for the treatment of 1 MGD of Stream 2 waste water. The pretreatment steps before the electrodialysis-reverse osmosis hybrid are the neutralization, solids removal, and carbon adsorption. A cost estimate of each step is made based on 1975 costs.

A. Pretreatment Design Bases

1. Neutralization and solids removal

A flow diagram and a material balance is given in Figure E-1. The feed contains 680 mg/l of Al^{+3} ion that results in 150 mg/l of suspended solids, $Al(OH)_3$ after neutralization. The primary settling tank underflow concentration of 500 mg/l at a flow of 0.3 MGD requires a surface area of 5600 ft^2. The sludge is thickened in a centrifuge at 1100 G's acceleration, to a 2 percent compacted sludge. The volume of the sludge is reduced to 75,000 GPD.

A capital and operating cost of this pretreatment step is given in Table E-1.

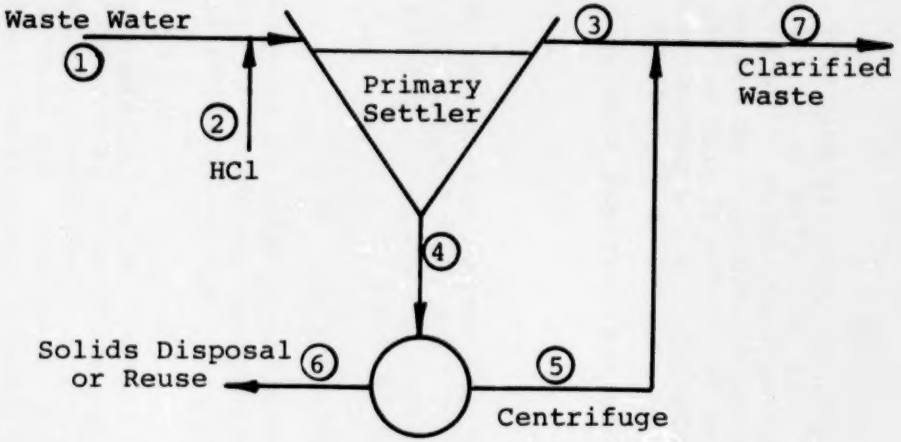
2. Carbon adsorption

The design basis and parameters of the carbon adsorption system for Stream 2 are given in Table E-2. The flow diagram and material balance are shown in Figure E-2. A summary of the capital and operating costs is given in Table E-3.

B. Electrodialysis-Reverse Osmosis Design

The design basis of the ED-RO hybrid for recycle of fresh water and concentrated brine from the pretreated Stream 2, is given in Table E-4. A flow diagram and material balance is shown in Figure E-3.

For the reverse osmosis unit, the capital is calcultated as 0.65 dollars per day permeate and the operating cost as 0.6 dollars per 1000 gallons of product water. For the electrodialysis unit, 6 presses, 1800 cell pairs each, are required. The cost per press of $500,000 times a factor of 2.5 gives the estimated capital cost. Membrane replacement is based on 7 years lifetime. A summary of capital and operating costs of the reverse osmosis-electrodialysis hybrid for Stream 2 recycle is given in Table E-5.



	Units	①	②	③	④	⑤	⑥	⑦
Al	lb./hr.	240	--	0	240	0	240	0
NaCl	lb./hr.	14,564	--	10,394	4,454	3,340	1,114	13,734
H_2O	lb./hr.	332,494	2,256	234,325	100,425	75,313	25,112	309,638
TOC	lb./hr.	30	--	21	9	8	1	29
HCl	lb./hr.	--	1,324	--	--	--	--	--
Total	lb./hr.	347,500	3,580	244,740	105,1246	78,844	26,282	323,584
Total	$\overline{M}$ gpd	1.0	0.0103	0.7072	0.3031	0.227	0.076	0.934
	Sp Gr	1.02	1.19	1.02	--	1.02	--	1.02
NaOH	lb./hr.	1,720	1.0103	--	--	--	--	--

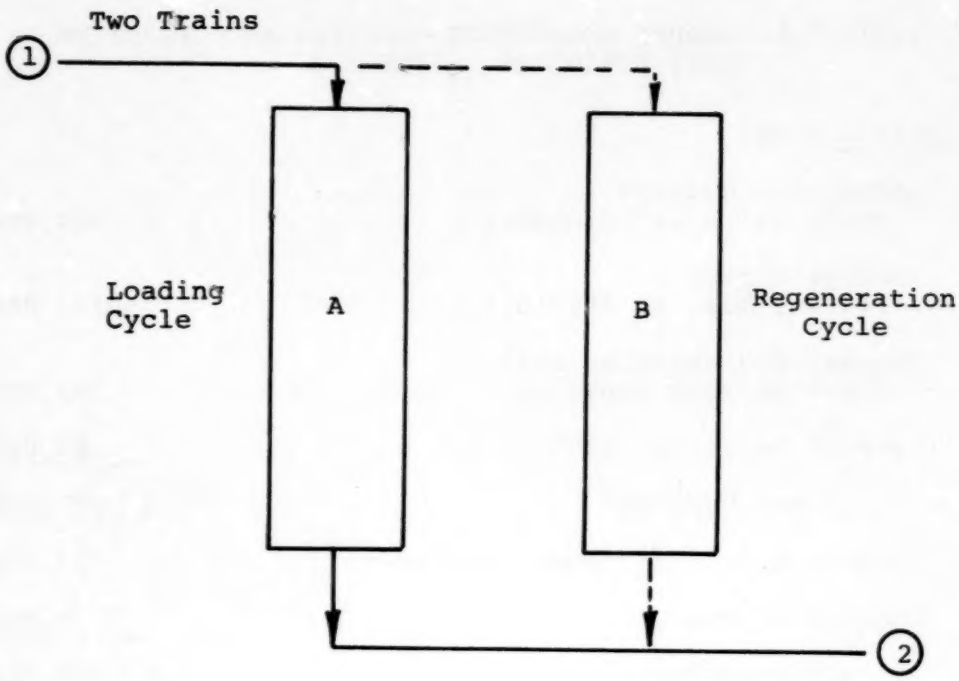
Figure E-1. NEUTRALIZATION AND SOLIDS REMOVAL - STREAM 2
Flow Diagram and Material Balance

Table E-1. NEUTRALIZATION AND SOLIDS REMOVAL - CAPITAL AND OPERATING COST ESTIMATES - STREAM 2

Capital Cost:		
Mixing Tank - rubber lined, 4×10^5 gallons	$ 54,000	
Pumps, Monel	16,000	
Gravity Thickener	75,000	
Centrifuges	50,000	
G&A (10%)	20,000	
Direct Capital	$215,000	
Allocated Capital, power	20,000	
Factory Expense (7%)	15,000	
FIXED CAPITAL	$250,000	
Operating Cost:	$/yr.	
Raw Materials		
HCl 37%, 3.4×10^6 lb./yr.	$ 68,000	
Maintenance (6%)	15,000	
Power	10,000	
Factory Expense (2.6%)	6,500	
Taxes and Insurance (1.1%)	2,700	
Depreciation (10%)	21,500	
	$123,700	$/yr.

Table E-2. CARBON ADSORPTION OF STREAM 2 - DESIGN BASIS

Feed Concentration TOC	-	90 mg/l
Effluent TOC	-	18 mg/l
Flow Rate	-	4.0 gpm/ft.^{2}
Columns - 4, 2 trains	-	20' x 18' diameter each
Bed Volume	-	2,430 cu. ft.
Weight Carbon (Witco 517)	-	60,750 lb./bed
Service Time	-	713 hours
Capacity	-	13.5 lb. TOC/lb. carbon
Regeneration Capacity	-	8,200 lb. carbon/day



	Units	1	2
TOC	lb./hr.	74.5	3
NaCl	lb./hr.	6,867	6,867
Water	lb./hr.	754,819	154,819
Total	lb./hr.	161,700	161,700

Figure E-2. FLOW DIAGRAM AND MATERIAL BALANCE FOR CARBON ADSORPTION TREATMENT - STREAM 2

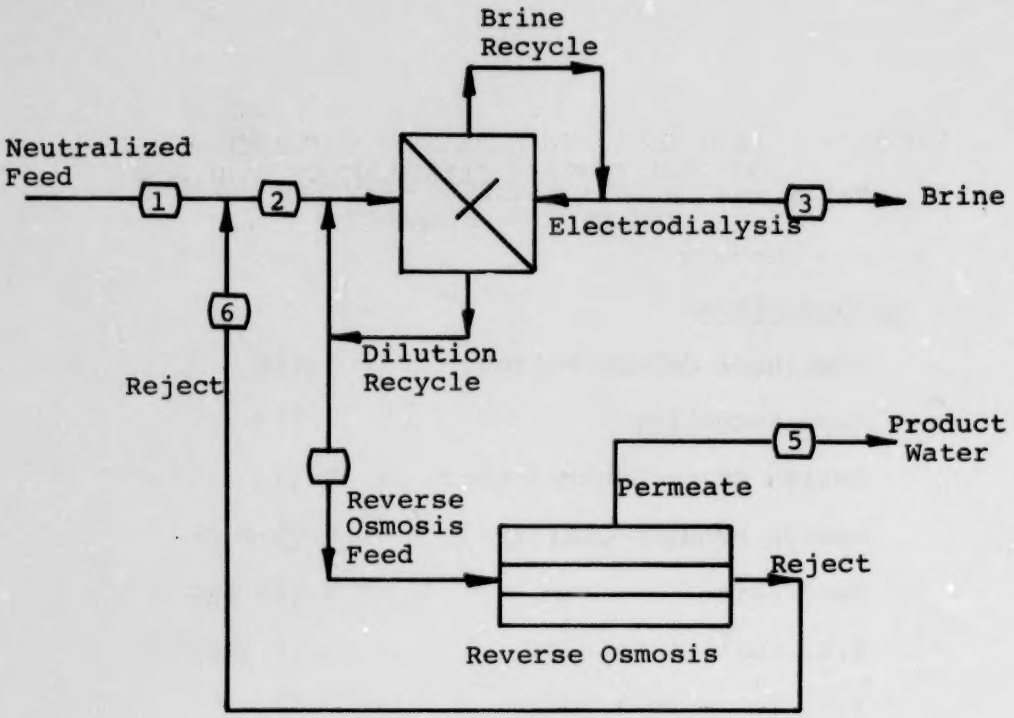
Table E-3. CARBON ADSORPTION - CAPITAL AND OPERATING COST ESTIMATES - STREAM 2

Capital Cost:	
Adsorption Columns Four, 20' x 14' diameter	$ 224,000
Initial Carbon 244,000 lbs. at 50¢/lb.	122,000
Thermal Regeneration Unit 8,200 lb./day capacity	492,000
General Services (10%)	84,000
Direct Capital	$ 922,000
Allocated Capital, power and steam	20,000
Factory Expense (7%)	65,000
FIXED CAPITAL	$1,017,000
Operating Cost:	$/yr.
Utilities	$ 40,000
Labor and O.H.	70,000
Carbon Make-up (7%)	100,000
Maintenance (6%)	60,000
Factory Expense (2.6%)	26,000
Taxes and Insurance (1.1%)	11,000
Depreciation (10%)	100,000
	$ 407,000

Table E-4. ELECTRODIALYSIS - REVERSE OSMOSIS TREATMENT - STREAM 2

Design Basis:

Feed NaCl Concentration	-	4.24%
Feed Normality	-	0.74 N
Design Brine Concentration	-	2.39 N
Design Product Quality	-	<500 mg/l
Feed Rate	-	0.934 mgd
E.D. Current Density	-	1.95 amp/dm^2
E.D. Volts/cell pair	-	0.55
R.O. Product Recovery	-	55%
R.O. NaCl Rejection	-	97%
No. of SS-O Presses	-	6
No. of Cell Pairs	-	10,800



	Units	①	②	③	④	⑤	⑥
NaCl	lb./hr.	13,734	15,520	13,730	1,790	30	1,700
H_2O	lb./hr.	309,638	474,480	94,270	380,210	215,348	164,922
Total	lb./hr.	323,378	490,000	108,000	382,000	215,378	166,622
Flow	mgd	0.934	1.410	0.31	1.10	0.62	0.480

Figure E-3. ELECTRODIALYSIS-REVERSE OSMOSIS TREATMENT - STREAM 2
Flow Diagram and Material Balance

Table E-5. COST ESTIMATE SUMMARY - ELECTRODIALYSIS REVERSE OSMOSIS TREATMENT OF STREAM 2

Reverse Osmosis:		
Capital	$ 403,000	
Operating Cost	122,760	
Electrodialysis:		
Capital	$7,500,000	
Operating Cost		
Power	377,800	
Membrane Replacement	294,000	
Total Labor	68,250	
Miscellaneous	150,000	
Depreciation	750,000	
Total	$1,640,050	$/yr.
ED-RO:		
Total Capital	$7,903,000	
Total Operating Cost	$1,763,000	$/yr.